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The Infrared Absorption by Hydrogen Sulfide

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Two of the bands in the spectrum of H_2S identified as ν_3 and ν_2 have been remeasured under high dispersion. The center of the band identified as ν_3 is found to be 2685 cm^{-1} and is a type of band showing no single Q branch at the center and is therefore ascribed to an oscillation of the electric movement along the axis of the intermediate moment of inertia. The fundamental ν_2 has been remeasured with two different gratings of different resolving power. It has been found to be of the type displaying a broad and partially resolved Q branch at the center and is henceforth identified with an oscillation of the electric moment along the axis of smallest moment of inertia. An estimate of the values of the moments of inertia has been made and these are found to agree well with those given by Cross, but the data here presented is interpreted as evidence for a model where the vertex angle is 85° rather than 92° as given by Cross.

I. INTRODUCTION

THE absorption in the infrared by the hydrogen sulfide molecule, presumably a nonlinear triatomic molecule similar to water vapor, has been studied by a number of investigators.[1] Absorption bands, enumerated in the order of their intensities, have been located at approximately the following frequency positions: 1260 cm^{-1}, 3795 cm^{-1}, 2685 cm^{-1}, 9911 cm^{-1}, 10,100 cm^{-1}, and 2615 cm^{-1}. All of these except the last, which has been found only in the Raman spectrum, have been measured under high dispersion and have been given the following identification, using Dennison's notation:[2] ν_2, $\nu_2+\nu_3$, ν_3, $3\nu_1+\nu_3$, $3\nu_3+\nu_1$ and ν_1, where the frequency ν_3 is perpendicular to the bisector of the apex angle and where ν_1 and ν_2 are along it. In general the frequencies ν_1 and ν_3 take values relatively high compared with ν_2. From an analysis of the rotational structure of the high frequency combination bands at 9911 and 10,100 cm^{-1} Cross has arrived at certain values of the moments of inertia and has inferred that the vertex angle must be slightly in excess of 92°. This would mean that ν_3 would lie along the axis of least moment of inertia while ν_1 and ν_2 would lie along the axis of the intermediate moment of inertia. According to the charts prepared by Dennison on the appearance of infrared bands of asymmetrical type molecules, ν_3 should then present a rotational structure containing a rather broad Q branch while ν_1 and ν_2 should be expected to display an absence of such a Q branch. The band taken to be the fundamental ν_3 is one of the bands measured by Nielsen and Barker and does not appear to give evidence of any Q branch whatever. It has been suggested that this band must have another half which might lie to higher or to lower frequencies. This belief was somewhat further strengthened by the measurements made by Rollefson on the band near 8.0μ interpreted as

[1] A. H. Rollefson, Phys. Rev. **34**, 604 (1929); W. Mischke, Zeits. f. Physik **67**, 106 (1931); H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931); H. H. Nielsen and A. D. Sprague, Phys. Rev. **37**, 1183 (1931); P. C. Cross, Phys. Rev. **47**, 7 (1935).
[2] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

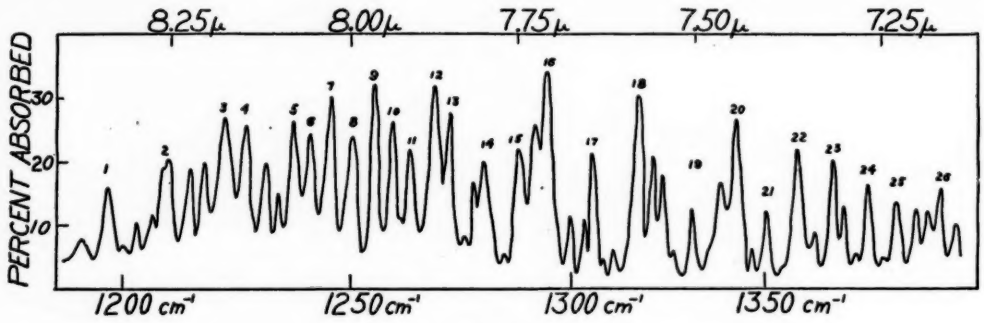

FIG. 1.

ν_2 and which gave evidence of a minimum near the center. It has therefore seemed important to remeasure these two absorption regions and in the 3.7μ region to extend the measurements well beyond the limits at both ends of the region as shown in the work of Nielsen and Barker. This has been the purpose of this investigation.

II. Experimental Work

The hydrogen sulfide gas used in making these measurements was obtained in tanks from the Ohio Chemical and Manufacturing Company in Cleveland. To insure that the gas was free from water vapor and carbon dioxide the gas was collected in a trap surrounded by liquid air and then fractionally distilled into the evacuated absorption cell. For both regions the same cell was used. It was made from a glass tube five centimeters in diameter and thirty centimeters long closed at the ends by windows of polished rocksalt.

For making the measurements a spectrometer of the usual design was available. Three echellette gratings ruled by R. W. Wood were used, one with 3600 lines per inch for the 3.7μ region and two others with 800 lines per inch and 2000 lines per inch for the region near 8.0μ. It was found feasible in each case to use slit widths equivalent to a spectral breadth of about 0.5 cm^{-1} and deflections were taken along the circle at these intervals.

III. Experimental Results. The 3.7μ Region

This is one of the two regions originally mapped by Nielsen and Barker. This region has here been carefully remeasured from 3.57μ to 3.83μ and these measurements extend beyond the region measured by Nielsen and Barker at each end by about 50 cm^{-1}. In none of the sets of data taken could anything be found in addition to that shown in the original work by these authors. Bailey, Thompson and Hale, in a recent article[3] have reported an absorption maximum at a slightly shorter wave-length than this and have suggested that the -7 line reported in Nielsen and Barker's work is to be interpreted to be a weak Q branch. This view we can definitely not ascribe to since then what we have observed must be only one branch. As we have already pointed out we can find no evidence of any other half of this band and what further absorption that may be found on either side of what we have measured is certainly far less intense and can hardly be identified as another branch. Moreover it would seem extremely difficult to account for a Q branch having a relative intensity as small as that of line -7 reported by Nielsen and Barker. Moreover no evidence of the frequency 2615

TABLE I. *The 8.0μ region under low dispersion. Wave numbers and wave-lengths.*

Line No.	Frequencies in cm^{-1}	Line No.	Frequencies in cm^{-1}
1	1196.8	14	79.6
2	1209.6	15	87.5
3	21.1	16	93.8
4	26.3	17	1304.5
5	35.9	18	16.8
6	40.3	19	30.4
7	44.2	20	41.2
8	48.7	21	48.5
9	54.1	22	56.4
10	58.2	23	66.0
11	62.3	24	74.6
12	67.8	25	82.3
13	71.1	26	94.5

[3] C. R. Bailey, J. W. Thompson and J. B. Hale. J. Chem. Phys. **4**, 625 (1936).

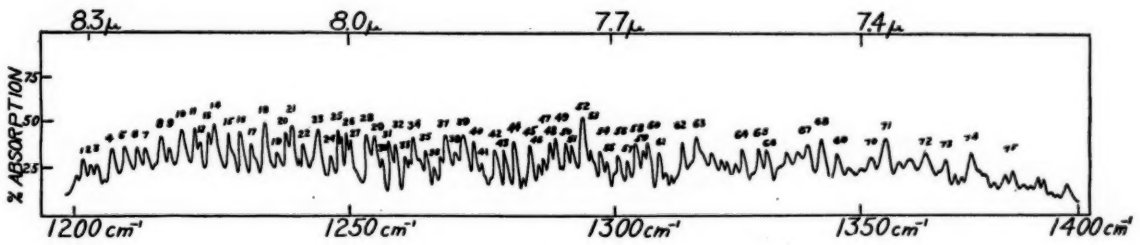

FIG. 2.

cm^{-1} was to be found. The band appears then to have its center at about 2685 cm^{-1} instead of 2630 cm^{-1} and in our opinion very definitely does not show a Q branch. This band must therefore be ascribed to an oscillation of the electric moment along the axis of the intermediate moment of inertia. These measurements are not shown graphically since they repeat almost exactly those given in the work of Nielsen and Barker; neither has any tabulation of frequency and wave-length positions of the lines been included, these also being in excellent agreement with the values given by them.

THE 8.0μ REGION

This band, originally reported by Rollefson, has here been remeasured under two different dispersions, one about equivalent to that available to Rollefson and one approximately three times as large. Under the lower dispersion the lines found in general agree well with the positions of lines reported by Rollefson, although in many cases the intensities of these are quite different. In fact, the appearance of the band is an entirely different one, in the present case there being no evidence of any minimum near the center, but rather the opposite.[4] At what appears to be the center of the band there occurs a broad line of appreciably greater intensity than any of its neighbors. The average spacing between principal lines seems to be about 10 cm^{-1}, very nearly that found between lines in the band at 2.7μ by Nielsen and Barker and by Cross at 10,100 cm^{-1} between lines arising from his $J_J \rightarrow J_J+1$ transitions. This spacing appears to be about ten percent larger than the spacing between lines at 3.7μ. The absorption pattern delineating those characteristics that repeated in the many runs made are shown in Fig. 1 and the frequencies of the principal lines measured under low dispersion are set down in Table I. It was found necessary to guard against falsification by water vapor in the atmosphere. This was accomplished by taking readings with the cell containing the gas in the beam, then with the evacuated cell in the beam, and comparing. Also as a further check, the deflections obtained with the evacuated cell in the beam were plotted underneath the percentage absorption curve to see that there was no consistent agreement between the absorption peaks apparently due to gas and the absorption peaks due to the atmosphere. The impression which this band leaves with us is that it resembles the band measured by Nielsen and Barker at 2.7μ in its rotational characteristics and also those reported by Cross much more than it resembles the band at 3.7μ. As its center we have chosen 1290 cm^{-1}, the position of the most intense of the lines in the band which we believe to be a Q branch.

When this region is examined using the grating ruled with 2000 lines per inch a great many new details in the absorption pattern become discernible. The absorption pattern, which has consistently repeated itself in the smallest details, is shown in Fig. 2. At a glance the two curves, Fig. 1 and Fig. 2, appear quite dissimilar but upon careful comparison of the one to the other, the general features of the two will be seen to be the same. Some uncertainty concerning the positions of some of the lines on the high fre-

[4] In the work by Nielsen and Barker mention was made of the fact that in a set of preliminary grating measurements made by Professor Barker on this region an absorption pattern was obtained, but in subsequent trials nothing was to be found. The above measurements have been compared with the aforementioned run and the two have been found to agree almost exactly with each other. The fact that nothing was to be found in the subsequent runs referred to in this earlier work can be interpreted only as meaning that the monochrometer preceding the spectrometer was out of proper adjustment while these measurements were made.

quency side must be allowed, due again to falsification by atmospheric water vapor lines. This falsification is much more difficult to compensate for here than when the dispersion is lower. Table II lists the frequency and wave-length positions of the most important peaks in the band.

Also here the most intense part of the band is at 1290 cm^{-1} and more even than before does this line appear to be a broad and partly resolved Q branch. We shall therefore interpret this band as arising from a vibration along the axis of least moment of inertia.

IV. Discussion of Experimental Results

The evidence obtained by these measurements seems to indicate that some modification of the model suggested by Cross, which has as the axis of least moment of inertia a line normal to the bisector of the apex angle, is necessary. There can be little doubt concerning the identification of the vibration frequency 1290 cm^{-1} as ν_2 since this frequency must be a relatively small one. Since, however, this band shows a Q branch, ν_2 must be a vibration along the axis of least moment of inertia, a condition which can be fulfilled only provided the apex angle be less than 88° 16′. Moreover for the frequency 2685 cm^{-1}, which in our opinion definitely shows no Q branch, to be ν_3 it must be required to be a vibration along the axis of the intermediate moment of inertia. This again indicates an apex angle of less than 88° 16′.

It is now necessary to reexamine the identification of the other bands known to exist in the infrared spectrum of hydrogen sulfide. The frequency of any band will in general be given by the relation $\nu=n_1\nu_1+n_2\nu_2+n_3\nu_3$ where, according to Dennison, when n_3 is odd the electric moment will be induced in a direction normal to the bisector of the apex angle, but will be along the bisector when n_3 is even. On the basis of such a model as we propose, namely one for which the vertex angle is less than 88° 16′, and taking the Raman line 2615 cm^{-1} as ν_1, 1290 cm^{-1} as ν_2 and 2685 cm^{-1} as ν_3 it is evident that the band centered at 3790 cm^{-1} and showing a Q branch can no longer be $\nu_2+\nu_3$, as suggested by Mecke,[5] and Cross, since with $n_3=1$, an odd integer, the vibration would be along the axis of the intermediate moment of inertia. It would then show no Q branch. This band might, however, be set equal to $\nu_1+\nu_3$. Likewise the frequencies 9911 cm^{-1} and 10,100 cm^{-1} are of the type in which Q branches occur and on the basis of our proposed model they must be redefined. We suggest that they may be set equal to $2\nu_3+2\nu_1$, and $2\nu_2+3\nu_1$, say, rather than to $\nu_3+3\nu_1$, and $3\nu_3+\nu_1$ as suggested by Cross. In fact these values agree a little better numerically, especially since ν_3 must be taken to be 2685 cm^{-1} rather than 2630 cm^{-1}. In Table III is summarized the manner in which we have identified the observed bands.

It would be of interest if the actual value of the apex angle of the molecule could be computed. This could of course be accomplished if the

[5] R. Mecke, Zeits. f. physik. Chemie **16**, 431 (1932).

Table II. *The 8.0μ region under high dispersion. Wave numbers and wave-lengths.*

Line No.	Frequencies in cm^{-1}	Line No.	Frequencies in cm^{-1}
1	1203.9	39	1270.3
2	04.7	40	71.9
3	05.7	41	73.3
4	08.1	42	76.1
5	10.3	43	78.1
6	12.3	44	79.9
7	13.3	45	81.2
8	16.1	46	84.3
9	17.6	47	85.4
10	19.9	48	86.6
11	21.9	49	87.5
12	23.0	50	90.0
13	24.3	51	91.1
14	25.3	52	93.4
15	27.6	53	94.4
16	29.4	54	96.7
17	32.1	55	97.8
18	34.4	56	99.8
19	36.4	57	1302.1
20	38.2	58	03.6
21	38.9	59	05.0
22	41.0	60	05.9
23	43.2	61	08.2
24	45.9	62	12.6
25	47.1	63	15.5
26	48.4	64	23.8*
27	49.3	65	27.6
28	52.5	66	30.2
29	53.7	67	39.6
30	54.7	68	41.4
31	55.7	69	43.9
32	57.0	70	52.6
33	59.0	71	55.5
34	60.9	72	64.6
35	63.2	73	69.1
36	64.4	74	74.2
37	67.0	75	83.3
38	68.5		

* From this point on, intense atmospheric water vapor absorption peaks occur from time to time and for this reason the positions of the absorption lines due to H_2S as given may indeed be slightly in error.

TABLE III. *Identification of observed bands.*

COMBINATION	FREQUENCY IN cm^{-1}	COMBINATION	FREQUENCY IN cm^{-1}
ν_1	2615 cm^{-1}	$\nu_1+\nu_2$	3970 cm^{-1}
ν_2	1290	$2\nu_3+2\nu_1$	9911
ν_3	2685	$2\nu_2+3\nu_1$	10100

correct values of the moments of inertia could be determined. The values I_A, I_B, and I_C as determined by Cross from his analysis of the two high frequency combination bands seem very convincing indeed, also in the light of our data even though no exact rotational analysis has been made. This may be seen in the following manner. Two quite different types of bands have been observed, namely that at 3.7μ and the other to which we believe those at 2.7μ and 8.0μ belong. The separation between the lines is, however, nearly the same in both types, about 9.0 cm^{-1} and 10 cm^{-1}, respectively. If we approximate the hydrogen sulfide molecule by a rotator where the moments of inertia are $A=B=C/2$ we should expect to find all the bands in the spectrum to be of the perpendicular type with the spacings between their lines identical. From Dennison's charts, however, it is seen that for a vibration along A there will develop a crowding together toward the center of the component lines in the band to form a Q branch as A is made less than B. Moreover, for an oscillation along B quite the opposite effect is to be observed as A is decreased with respect to B. Now clearly the value of Dennison's parameter of asymmetry ρ defined as A/B cannot be much less than 0.9 since at least under not too high dispersion some semblance of regularity in the rotational structure is maintained. Approximating the hydrogen sulfide molecule then by a symmetric rotator where $A'=B'=1/[(A+B)/2]$ and $C'=2A'$ and remembering that prominent lines (i.e., the Q branches of the component bands of the perpendicular band) will arise from transitions of the type $\Delta J=0$, $\Delta K=\pm 1$ we obtain as the spacing between any two lines $\Delta\nu=h/[4\pi^2(A+B)]$. Taking as the value for $\Delta\nu$ the average spacing in the two types of observed bands and letting $A=0.9B$ we obtain $A=2.7\times10^{-40}$ g cm^2, $B=3.1\times10^{-40}$ g cm^2 and $C=5.8\times10^{-40}$ g cm^2, in good agreement with the values $I_A=2.667\times10^{-40}$ g cm^2, $I_B=3.076\times10^{-40}$ g cm^2, and $I_C=5.845\times10^{-40}$ g cm^2 given by Cross. These values for the moments of inertia, when the axis of the smallest moment of inertia is taken along the bisector of the apex angle, lead to a value for the apex angle of about 85°.[6, 7]

It is interesting to compare the fundamental bands here observed with the fundamentals observed in the spectrum of water vapor. In the water vapor molecule where the vertex angle appears to be about 104° the axis of smallest moment of inertia is normal to the bisector of the apex angle. The low frequency of vibration ν_2 along the bisector of the vertex angle has here been identified as the observed frequency 1595 cm^{-1} and its position in the spectrum as well as its rotational character is consistent with such an identification. The frequency ν_3, a high frequency vibration normal to the bisector of the apex angle, has been taken as the observed frequency 3756 cm^{-1}, and also its position in the spectrum and its rotational character are in agreement with such an identification. This leaves the Raman frequency 3604 cm^{-1} to be taken as ν_1. Hence the observed fundamentals found in the spectrum of hydrogen sulfide are entirely analogous to those found in the spectrum of water vapor.

[6] Further evidence in support of such a model will be produced by A. H. Nielsen and H. H. Nielsen in an article soon to appear dealing with the spectrum of D_2S and HDS.

[7] The value of the vertex angle of 110° given by Bailey, Thompson and Hale as determined from their work seems to us as hardly compatible with the evidence gained from a study of the rotational structure of these bands. Quite aside from the question of whether the molecule is an obtuse or an acute angle isosceles triangle, the ratio of the moments of inertia assumes an impossible value for such a model. Computing the value of the parameter ρ defined above from Bailey, Thompson and Hale's 110° model one obtains a value $\rho=0.45$ and that this is a value much too small is readily seen by an examination of the diagrams prepared by Dennison. These show that for one of the band types, for a value of $\rho=0.5$ the Q branches are already quite sharp and by far the most intense lines in the bands while in the other type of band a definite absence of lines at the center of the band is to be expected. This can hardly be said to be what is observed experimentally. Moreover, the regularity in the rotational structure observed in the H_2S bands at low dispersion and especially the fact that the spacings between lines is almost the same in both types of bands seems incoherent with a value of ρ much less than 0.9.

The Analysis of the Raman Spectra of $Si_2Cl_6(l)$ and of $Si_2H_6(g)$*

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The Raman spectra of $Si_2H_6(g)$ and of $Si_2Cl_6(l)$ have been photographed. Polarization measurements of the stronger lines of Si_2Cl_6 have been made. From a consideration of the relations among the modes of vibration of similar molecules having different symmetry, the analysis of the observed lines is facilitated by a knowledge of the assignments of the fundamental frequencies of SiH_4, $HSiCl_3$ and $BrSiCl_3$. A definite assignment is made for the three observed lines of Si_2H_6. A tentative assignment of the observed lines of Si_2Cl_6 is made and some evidence is presented for the existence of internal rotation in this molecule at room temperature.

IN addition to determining and assigning some of the fundamental vibration frequencies of disilane and of disilicon hexachloride, we have attempted in this investigation to determine whether or not internal rotation is present in the Si_2Cl_6 molecule at room temperature.

EXPERIMENTAL

The disilane used was obtained from Professor Johnson of the University of Chicago, and we wish to express our gratitude to him for his kindness in making the material available to us. It was quite pure, showing, according to Professor Johnson, a molecular weight of 62.6; the formula weight is 62.2.

The disilicon hexachloride was prepared by treating ferrosilicon[1] with chlorine and fractionally distilling the product four or five times. It boiled at 145°±0.5°.

The spectrum of gaseous disilane was photographed with radiation from a mercury arc. A Pyrex Raman tube was used to avoid possible decomposition since Hg 2537A was found to decompose SiH_4.[2] When the Si_2Cl_6 was photographed in a Pyrex tube without a filter it showed some decomposition with the appearance of small brown flakes of silicon. An acid quinine chloride solution as filter absorbed almost completely all lines of the mercury arc of higher frequency than the Hg 4358 group, and no decomposition occurred. As Raman lines excited by the 4047 group were observed in the absence of the filter, the decomposition was probably due to the Hg 3650 group.

FIG. 1. Experimental arrangement for polarization measurements. *M*, half-wave mica plate; *N*, Nicol prism; *S*, step weakener on slit of spectrograph; *T*, Raman tube; *L*, condensing lens; *B*, parallel black screens.

Polarization measurements were made on the stronger lines of Si_2Cl_6 (*l*). The experimental arrangement used for these measurements is shown in Fig. 1. This arrangement suffers the disadvantage that a separate exposure must be made for the parallel and perpendicular components,[3] but possesses the two following important advantages: (1) The use of a step weakener on the slit[4] automatically calibrates the photographic plate, the blackening along the length of each spectral line varying in steps of known relative intensity of illumination. Thus both the source and the exposure time for calibration are the same as for the image, an important factor where low intensities and long exposure times are involved. (2) The use of a half-wave mica plate[5] preceding

* Contribution from the Gates and Crellin Laboratories of Chemistry of the California Institute of Technology, No. 574.

[1] Quig and Wilkinson, J. Am. Chem. Soc. **48**, 902 (1926); Martin, J. Chem. Soc. **105**, 2836 (1914).

[2] Stitt and Yost, J. Chem. Phys. **4**, 82 (1936).

[3] An arrangement eliminating this disadvantage is obtained if, in Fig. 1, *M* and *N* be removed and a large aperture Wollaston prism be introduced into the collimator tube of the spectrograph. Correction for polarization due to the spectrograph may then be eliminated by rotating the Wollaston 45° about the axis of the tube from the position in which the two beams emerging from it are in a vertical plane. The mercury arc is placed so that with the Raman tube it determines a plane at 45° to the vertical. This arrangement was not used because a suitable Wollaston prism was not available.

[4] We are indebted to Professor Houston and Dr. C. M. Lewis for allowing us to use a step weakener made by them. See Phys. Rev. **44**, 903 (1933).

[5] We are indebted to Dr. John Strong for suggesting the use of a half-wave plate.

the Nicol prism eliminates the correction for polarization due to the apparatus, and also allows each component to be photographed passing through the spectrograph with the electric vector in the horizontal plane, thus minimizing the loss due to reflection by the prism faces.

For photographing one component (the ‖-component for illumination in a vertical plane) the axis of the Nicol prism is horizontal and the axis of the mica plate parallel to that of the Nicol. The only alteration necessary for photographing the other component is to rotate the half-wave plate through 45°, thus rotating by 90° the electric vector of the light passing through it. Tests showed that a 0.048 mm mica sheet serves as a half-wave plate with practically no error from 4400A to 5000A. Only for high frequency shifts from Hg 4358A as an exciting line need a different thickness plate be used.

The step weakener was calibrated at a number of different wave-lengths. For the calibration a low voltage Mazda lamp, such as used in street lights, served as constant source of illumination, and the small, spiral, vertical filament served as a good point source. The inverse square law of illumination was assumed throughout. Five positions giving relative intensities of 1, 0.8, 0.6, 0.4, 0.2 were used, each with exactly one hour exposure time. By microphotometering these continuous spectra at any wave-length the calibration for that wave-length could be made. Eight steps were used having relative transmission values of 1.00, 0.85, 0.61, 0.45, 0.34, 0.26, 0.19, 0.14 at 4384A.

TABLE I. *Raman spectrum of Si_2H_6 (g). Pressure approximately 2 atmos.*

$\Delta\tilde{\nu}$ IN cm^{-1}	NO. OF EXCITING LINES	DESCRIPTION
2163	6	Strong; sharp.
910 to 955	2	Weak; diffuse.
434.5	3	Medium intensity; sharp; appeared also as an anti-Stokes line.

A Raman tube of rectangular cross section was employed in order to minimize reflection of incident light. Parallel black screens for making the incident light approximately parallel were so spaced that only light within about 15° of the vertical could enter the Raman tube. For $\rho=0.86$ the error in ρ is less than 0.02 for incident light at an angle of 20° with the vertical.[6] Eastman I−O plates were used.

The mercury arc was run at constant voltage and showed little fluctuation in current over long periods of time. A 48-hour exposure of each component was taken, the illumination probably being very nearly the same for both components. However, it should be pointed out that, for this work, it is not necessary that the illumination be precisely the same for the two components for accurate results. For practically all compounds

[6] G. Placzek, "Rayleigh-Streuung und Raman-Effekt," *Handbuch der Radiologie*, Band II, Teil 2 (Leipzig, 1934), p. 244.

TABLE II. *Raman spectrum of Si_2Cl_6 (l). (Anti-Stokes lines not included.)*

ν IN cm^{-1}	$\Delta\tilde{\nu}$ IN cm^{-1}	RELATIVE INTENSITY	POLARIZATION RATIO (ρ)	DESCRIPTION
22806	124	8	0.72±0.02	Double line; diffuse. Not resolved in polarization measurements. 132 cm^{-1} portion seems slightly less diffuse than 124 cm^{-1} portion.
22814	132	5		
22759	179	~0.4		Sharp.
22726	212	4	0.86±0.02	Sharp.
22685	354	<<1	—	Hg 4047 as exciting line.
22641	354	<<1		Hg 4339 as exciting line.
22584	354	10	<0.05	Sharp.
22561	377	1		Double; similar to 124, 132 cm^{-1} doublet. 388 cm^{-1} portion seems slightly more intense and less diffuse than 377 cm^{-1} portion.
22551	387			
22517	421	<<<1		Broad; too broad to be $\Delta\nu=425$ cm^{-1} of $SiCl_4$.
22478	460	<<<1		Very weak; moderately diffuse.
22451	487	<<<1		Very broad. Strongest of <<<1 lines. Too intense to be $\Delta\nu=588$ cm^{-1} from Hg 4339.
22405	590	<<<1		Hg 4347 as exciting line.
22373	565	<<1		Moderately diffuse. Too intense for $\Delta\nu=625$ cm^{-1} from Hg 4347 as exciting line.
22348	590	3	0.88±0.03	Rather diffuse.
22313	625	2	<0.5	Moderately diffuse.
22232	706	<<<1		Very weak; moderately diffuse.

TABLE III. *Relations among the irreducible representations of certain symmetry groups.*

T_d	C_{3v}	C_3	D_3	D_{3h}	C_{3v} or D_3	D_{3d}
A_1 }	A_1 }	A	A_1	A_1' }	A_1	A_{1g}
A_2 }	A_2 }		A_2	A_2'' }		A_{2u}
E }	E }	$E_{1,2}$	E			
T_1 }	A_2+E			A_1'' }	A_2	A_{2g}
				A_2' }		A_{1u}
T_2 }	A_1+E			E' }	E	E_g
				E'' }		E_u

some Raman lines have $\rho=6/7$ for ordinary incident light. If the exposure is somewhat different for the two components, one may find an accurate correction factor to use with the observed ρ values from the fact that the highest ρ is probably actually 6/7. In the present work, the observed values for two lines were 0.86 within narrow limits thus confirming our assumption that the illumination was the same for the two exposures.

On plotting the microphotometer reading for each step as ordinate against the percentage transmission for that step as abscissa for each component, the depolarization ρ is the ratio of the abscissas for the same ordinate on the two curves. (Correction for background was unnecessary as the background was negligible. Note the background radiation also is reduced in known ratios.) The values of ρ thus found choosing different ordinates agreed quite well.

The experimental results are summarized in Tables I and II.

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Wigner[7] has shown that the normal coordinates for vibrations of a system of point particles belong to (that is, have the linear transformation properties of) definite irreducible representations (IR) of the point group representing the symmetry of the system. The methods for determining, for a given model, how many vibrational frequencies belong to each of the IR of the appropriate group and for determining the selection rules in the Raman and infrared spectrum are now well known.[8]

[7] *Göttingen Nachrichten* (1930), p. 133.

[8] See reference 6, 7; also E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934), J. Chem. Phys. **2**, 432 (1934) and references given there.

It is instructive to follow (*a*) how the fundamental frequencies for a model with a given number of atoms are distributed among the IR of the appropriate point group as the symmetry of the model is changed from that of one point group to that of another, and (*b*) and (*c*) how the new modes of vibration introduced when the number of atoms in a model is increased, with and without altering the point group symmetry, distribute themselves among the IR of the appropriate point group. The use of such considerations for correlation and assignment of frequencies is frequently very helpful. We will restrict ourselves here to a discussion of examples related to the interpretation of the spectra of Si_2H_6 and Si_2Cl_6.

For studying the distributions referred to in the preceding paragraph the methods already referred to[8] are employed, supplemented by some further considerations. When the symmetry is lowered to that of a subgroup of the original group, those IR of the original group possessing the same characters with respect to the operations of the subgroup merge to form a single IR of the subgroup. Mulliken[9] has published tables showing some of these relations. When the symmetry is altered so that the new point group is not a subgroup of the original one, a correlation between the two is then obtained by seeing how the IR of each reduce to those of the group possessing all elements of symmetry common to the two. For our present purposes we are interested in these relations for the point groups C_{3v}, D_3, D_{3d}, D_{3h}, and T_d; these are shown in Table III. IR designated by **A** are one dimensional, and frequencies associated with them are nondegenerate; those

TABLE IV. *Irreducible representations to which the fundamental frequencies of certain models belong, and selection rules for Raman and infrared spectra.*

FORMULA	SYMMETRY	FREQUENCIES	RAMAN ACTIVE	INFRARED ACTIVE
XY_3	C_{3v}	$2A_1$, 2E	$2A_1$, 2E	$2A_1$, 2E
XY_4	T_d	A_1, E, $2T_2$	A_1, E, $2T_2$	$2T_2$
XY_3Z	C_{3v}	$3A_1$, 3E	$3A_1$, 3E	$3A_1$, 3E
X_2Y_6	D_{2d}	$3A_{1g}$, A_{1u}, $2A_{2u}$ $3E_g$, $3E_u$	$3A_{1g}$, $3E_g$	$2A_{2u}$, $3E_u$
X_2Y_6	D_{3h}	$3A_1'$, A_1'', $2A_2''$ 3E', 3E''	$3A_1'$, 3E', 3E''	$2A_2''$, 3E'
X_2Y_6	D_3	$4A_1$, $2A_2$, 6E	$4A_1$, 6E	$2A_2$, 6E

Note: By active is meant only that a frequency is permitted to appear, and not that it necessarily does appear.

[9] Phys. Rev. **43**, 294 (1933).

designated with letters **E** and **T** are two and three dimensional, respectively, and the frequencies associated with them are doubly and triply degenerate.

In Table IV are shown the distribution of the fundamental vibrations for several models among the IR of the appropriate point group, and also the selection rules for the fundamentals in their infrared and Raman spectra. For those vibrations belonging to the completely symmetric IR ($\mathbf{A}_1$ of $\mathbf{D}_3$, $\mathbf{A}_1$ of $\mathbf{C}_{3v}$ and of $\mathbf{T}_d$, $\mathbf{A}_1'$ of $\mathbf{D}_{3h}$, and $\mathbf{A}_{1g}$ of $\mathbf{D}_{3d}$) the corresponding Raman lines have a polarization ratio $\rho<6/7$; for all others $\rho=6/7$.

In Table V are shown the Raman selection rules for first overtones and one-one combinations for these same models.

Coordinates belonging to appropriate IR for a given model of X_2Y_6 may be constructed readily from similar coordinates for the XY_3 model. (The normal coordinate for a given vibration is a linear combination of those symmetry coordinates belonging to the IR with which that vibration is associated.) The method is as follows: For each symmetry coordinate of XY_3 construct two for X_2Y_6. In both of these each $-XY_3$ radical vibrates with the XY_3 symmetry coordinate, but in one the two radicals vibrate in phase, in the other 180° out of phase. This will be made clear by reference to Fig. 2, in which are shown the symmetry coordinates thus[10] found from the symmetry coordinates formulated by Howard and Wilson[11] for XY_3. The "in phase" coordinates (those with subscript s) are unchanged by rotation about a twofold axis of the X_2Y_6 model,

TABLE V. *Raman selection rules for first overtones and for one-one combinations of fundamental frequencies of X_2Y_6 models. All are allowed except those shown.*

SYMMETRY	FORBIDDEN RAMAN LINES
$\mathbf{D}_3$	$\mathbf{A}_1+\mathbf{A}_2$
$\mathbf{D}_{3d}$	$(\mathbf{A}_{1g}$ or $\mathbf{A}_{1u})+(\mathbf{A}_{2g}$ or $\mathbf{A}_{2u})$, $\mathbf{A}_{1g}+\mathbf{E}_u$, $\mathbf{A}_{1u}+\mathbf{E}_g$, $\mathbf{A}_{2g}+\mathbf{E}_u$, $\mathbf{A}_{2u}+\mathbf{E}_g$.
$\mathbf{D}_{3h}$	$(\mathbf{A}_1'$ or $\mathbf{A}_1'')+(\mathbf{A}_2'$ or $\mathbf{A}_2'')$

[10] Slight modification of the XY_3 coordinate may be necessary to eliminate over-all rotation as in forming τ_s of Fig. 2 from ω_x, ω_y of XY_3, or to avoid distortion as in forming ω_x, ω_y of X_2Y_6 in Fig. 2 from $\mathbf{T}_x$, $\mathbf{T}_y$ of XY_3. We wish to thank Dr. J. B. Howard for calling our attention to this.

[11] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **3**, 630 (1934).

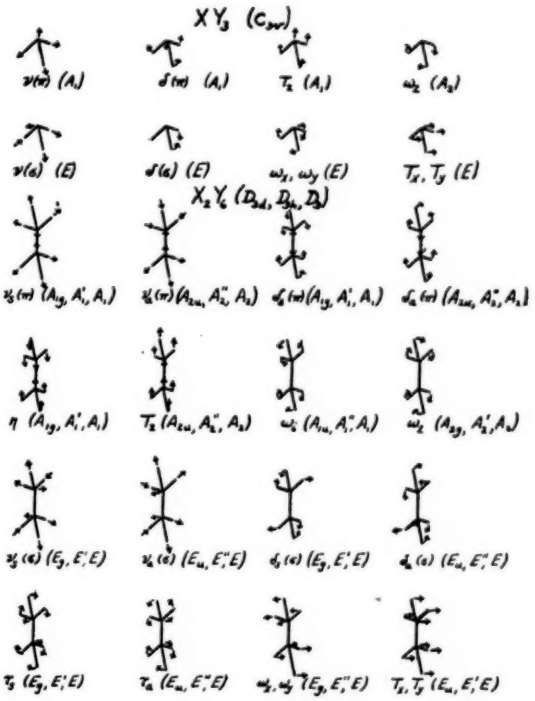

FIG. 2. Symmetry coordinates for X_2Y_6 from those for XY_3.

whereas the same operation changes the "out of phase" coordinates (those with subscript a) by 180° in phase. The equilibrium configuration for X_2Y_6 shown in Fig. 2 is that for symmetry $\mathbf{D}_{3d}$, but beneath each coordinate is noted the IR of the point groups $\mathbf{D}_{3d}$, $\mathbf{D}_{3h}$ and $\mathbf{D}_3$, respectively, to which the suitably drawn coordinate belongs when the $-XY_3$ radicals are combined to form molecules of these symmetries. These coordinates have been given designations for future reference.

In the following discussion we shall refer to these coordinates as if they were normal coordinates. The symmetry coordinates of $\mathbf{AB}_3$ have been chosen so that each one involves primarily a bending or a stretching of the bonds. For most $\mathbf{AB}_3$ molecules the large difference in the frequencies of the two vibrations belonging to either $\mathbf{A}_1$ or $\mathbf{E}$ of $\mathbf{C}_{3v}$ show that the normal coordinates are probably very similar to these symmetry coordinates. The same is probably true of the coordinates shown for $\mathbf{A}_2\mathbf{B}_6$. This would be expected to be true, especially for the degenerate modes, in case of free internal rotation.

Discussion

Si_2H_6

There is no question as to the presence of internal rotation in Si_2H_6. In ethane the difference in stability of the $\mathbf{D}_{3h}$ and $\mathbf{D}_{3d}$ configurations is considerably less than kT at room temperature so that the internal rotation is almost free.[12] In Si_2H_6, due to the greater distance between the two central atoms than in C_2H_6, rotation of the two halves of the molecule with respect to each other must be even less hindered than in ethane.

$\Delta\nu=2163$ cm^{-1} is doubtless due to $\nu_s(\pi)$ because of its great intensity, its sharpness, and its numerical proximity to $\nu(\pi)=2187$ cm^{-1} of SiH_4.[2]

$\Delta\nu=910$ to 955 cm^{-1} is probably $\delta(\sigma)$. In SiH_4 we have assigned[2] $\nu=910$ cm^{-1} to IR $\mathbf{T}_2$ of $\mathbf{T}_d$, $\nu=978$ cm^{-1} to $\mathbf{E}$ of $\mathbf{T}_d$, and of these two frequencies only $\Delta\nu=978$ cm^{-1} was observed with appreciable intensity in its Raman spectrum. On the assumption that the intensities of the Raman lines of Si_2H_6 are related to those of SiH_4, in accordance with Table III we conclude $\Delta\nu=910$ to 955 cm^{-1} of Si_2H_6 probably belongs to $\mathbf{E}$ of $\mathbf{D}_3$, hence is probably $\delta(\sigma)$ rather than $\delta(\pi)$.

$\Delta\nu=434.5$ cm^{-1} is very likely η. The fundamental frequencies of SiH_4 indicate that all the fundamental frequencies of Si_2H_6 are in the neighborhood of either 1000 cm^{-1} or 2000 cm^{-1} except η, ω_i and τ. ω_i is probably zero as nearly free internal rotation is present. η would be expected to be sharp, and perhaps of appreciable intensity because of its appearance in the Raman spectrum of C_2H_6 (g).[13] If it is assumed that 434.5 cm^{-1} is the frequency of vibration of two rigid $-SiH_3$ groups with respect to each other, a stretching force constant of 1.7×10^5 dynes/cm is found for the Si$-$Si bond.

Si_2Cl_6

In Si_2Cl_6 the situation as to internal rotation is not so clear. The electrostatic interaction due to assuming a positive charge of 4.5×10^{-10} e.s.u. on each Si atom and a negative charge of 1.5×10^{-10} e.s.u. on each Cl atom (corresponding to the high value of 3.0 Debyes for the dipole moment of the Si$-$Cl bond)[14] results in stabilizing the $\mathbf{D}_{3d}$ configuration by 475 cal./mole with respect to the $\mathbf{D}_{3h}$ configuration. The van der Waals attraction between the Cl atoms tends to stabilize the $\mathbf{D}_{3h}$ configuration by an amount of the order of 450 cal./mole.[15] Due to the mutual repulsion of the Cl atoms, there is a barrier of the order at 500 cal./mole between the two configurations.[16] Hence it seems probable that resistance to internal rotation at room temperature is probably of the order of $k\mathbf{T}$, the $\mathbf{D}_{3d}$ configuration being somewhat more stable than the $\mathbf{D}_{3h}$ one.

In accordance with Table IV we see that if Si_2Cl_6 possesses a rigid staggered ($\mathbf{D}_{3d}$) structure, six distinct fundamental frequencies are permitted in the Raman spectrum, three of which would have a polarization ratio $\rho<(6/7)$. If Si_2Cl_6 possesses a rigid structure having a symmetry plane perpendicular to the threefold axis, nine distinct fundamental frequencies are permitted to be Raman active, and three of these would have $\rho<(6/7)$.[17] If free internal rotation occurs the symmetry of the molecule is only $\mathbf{D}_3$ most of the time. For a rigid $\mathbf{D}_3$ model Table IV shows that ten distinct fundamental frequencies are permitted to be Raman active. However, if free rotation is present, one of these, ω_i, is zero, and intuitively it seems very likely that under such conditions the corresponding "in phase" and "out of phase" vibrations not symmetric with respect to the threefold axis (the degenerate vibrations) would become indistinguishable, thus resulting in only six distinct fundamental frequencies permitted in the Raman spectrum.

[12] Eucken and Weigert, Zeits. f. physik. Chemie **B23**, 266 (1933); Eucken and Parts, *Göttingen Nachrichten* (1932), p. 274; Zeits. f. physik. Chemie **B18**, 61 (1932); Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

[13] Teller and Topley, J. Chem. Soc. 885 (1935).

[14] Distances used: Si$-$Cl $=2.00$A, the $SiCl_4$ value. Si$-$Si $=2.34$A the value recently found in Si_2H_6 by electron diffraction. (Dr. Brockway, private communication.) The C$-$Cl dipole moment is about 1.5 Debyes and the Si$-$Cl separation is about twice the C$-$Cl separation on Pauling's electronegativity scale (See J. Am. Chem. Soc. **54**, 3570 (1932)).

[15] See Slater and Kirkwood, Phys. Rev. **37**, 682 (1931).

[16] If for the repulsive potential between two bound Cl atoms, the expression $\phi(r)=be^{(2\gamma_0-\gamma)/\rho}$ is used, with $b=10^{-12}$ erg, $\rho=0.2091$A, and $\gamma_0=1.370$A, the calculated barrier is about 350 cal./mole. These values of b and ρ were used to give the best fit for neon (see Bleick and Mayer, J. Chem. Phys. **2**, 252 (1934)) and γ_0 was chosen by comparison with γ_0 for neon and for the alkali and halide ions (see Huggins and Mayer, J. Chem. Phys. **1**, 643 (1933)). The barrier (exclusive of Coulomb interaction) calculated if the Cl atoms are assumed to be chloride ions is about 2000 cal./mole. (See Huggings and Mayer, above.) The correct value is probably nearer that calculated for bound chlorine atoms.

[17] By rigid here is meant that resistance to internal rotation is sufficiently great so that only small vibrations about the equilibrium position may occur.

In addition to the selection rules, we have some knowledge of the fundamental frequencies of $HSiCl_3$[18] and of $BrSiCl_3$[19] to aid us in our analysis of the Si_2Cl_6 spectrum. In Table VI are shown the observed Raman frequency shifts for these compounds and the assignment of the frequencies. The assignment shown for the $HSiCl_3$ frequencies is that of Mecke.[20] The analysis of the $BrSiCl_3$ frequencies we have made by analogy to Mecke's analysis[20] of the $HSiCl_3$, HCX_3 and CH_3X frequencies (X = halogen). The designations ν and δ refer to vibrations roughly approximated by the symmetry coordinates shown in Fig. 2 for XY_3 where X now becomes a rigid H−Si (or Br−Si) group, and $\eta(\pi)$ and $\eta(\sigma)$ refer, respectively, to vibrations in which the motion is essentially a stretching or a bending with respect to the $-SiCl_3$ group of the H−Si (or Br−Si) bond. Calculation of $\eta(\pi)$ for $BrSiCl_3$, assuming it to involve only a vibration of the Br atom relative to a rigid $-SiCl_3$ group and assuming the stretching force constant of the Si−Br bond to be unchanged from its value in $SiBr_4$, yields 314 cm^{-1}.

Considering both $BrSiCl_3$ and Si_2Cl_6 as a $-SiCl_3$ group with a rather large mass attached along the threefold axis, one would expect the $\nu(\pi)$ and $\delta(\pi)$ vibrations in one to be of approximately the same frequency as in the other. Without concluding as to the symmetry of Si_2Cl_6, this prediction coupled with the selection rules and the values of ρ for these lines lead us to assign 354 $cm^{-1} = \nu(\pi)$ and either 124 or 132 $cm^{-1} = \delta(\pi)$ in Si_2Cl_6.

Since the mass of the H atom is so small relative to that of Si or Cl, the frequencies of $HSiCl_3$ (omitting $\eta(\pi)$ and $\eta(\sigma)$)[21] are very nearly those of a free $-SiCl_3$ group. If nearly free internal rotation is present in Si_2Cl_6, the perpendicular vibrations $\nu(\sigma)$ and $\delta(\sigma)$ would be expected to be of nearly the same frequency as those of a free $-SiCl_3$ group, since then the net instantaneous momentum in any direction perpendicular to the threefold axis would be essentially zero for each half of the molecule. This condition need not obtain for a rigid[17] configuration. The appreciable intensity, the polarization ratio of 6/7, and the numerical value of 590 cm^{-1} in Si_2Cl_6 indicate that it is $\nu(\sigma)$. This proximity to the value of $\nu(\sigma)$ = 587 cm^{-1} in $HSiCl_3$ favors the conclusion that there is nearly free internal rotation in Si_2Cl_6. The appreciable intensity and ρ value of 212 cm^{-1} lead to its assignment as $\delta(\sigma)$. This is slightly higher than $\delta(\sigma)$ in either $HSiCl_3$ (179 cm^{-1}) or $BrSiCl_3$ (183 cm^{-1}).

We are unable to make definite assignments of more than these four lines as fundamental frequencies of Si_2Cl_6. The relation of these assignments to the analyses of the frequencies of $HSiCl_3$, $BrSiCl_3$ and $SiCl_4$ from the viewpoint of Table III is shown in Table VII.

Several of the weaker lines observed may be assigned as combinations or overtones:

421 cm^{-1}: The first overtone of 212 cm^{-1}.
487 cm^{-1}: Combination 132 cm^{-1}+354 cm^{-1}.
565 cm^{-1}: Combination 212 cm^{-1}+354 cm^{-1}.
706 cm^{-1}: First overtone of 354 cm^{-1}.

The remaining weak lines, $\Delta\nu$ = 377, 387 and 460 cm^{-1}, are also probably due to combinations or overtones. Numerically they agree with 124, 132 and 212 cm^{-1}, respectively, combining with a frequency of about 252 cm^{-1}. As fundamentals we can see no feasible assignment for them.

The component of the 124, 132 cm^{-1} doublet which is not $\delta(\pi)$ may well be τ with a polarization ratio of 6/7. The observed ρ = 0.72 is an over-all value for both lines.

Two possibilities suggest themselves for 179 cm^{-1}: (1) It may be η; (2) If the correct configuration is a rigid[17] one, it may be $\delta_a(\sigma)$, its numerical value being practically the same as $\delta(\sigma)$ in $HSiCl_3$ and $BrSiCl_3$. If η is assumed to be the vibration of two rigid $-SiCl_3$ groups with respect to each other, and if the Si−Si bond stretching

TABLE VI. *Assignment of the fundamental vibration frequencies of $HSiCl_3$ and of $BrSiCl_3$.*

$HSiCl_3$		IR	DESIGNATION	$BrSiCl_3$
489	(6.6)	A_1	$\nu(\pi)$	362 (V. STR.)
249	(2.6)	A_1	$\delta(\pi)$	123
2256	(8.3)	A_1	$\eta(\pi)$	325
587	(1)	E	$\nu(\sigma)$	410
179	(4)	E	$\delta(\sigma)$	183 (STR.)
797	(1)	E	$\eta(\sigma)$	201

[18] de Hemptinne and Peeters, Bull. Sci. Acad. Roy. Belg. **17**, 1107 (1931); Urey and Bradley, Phys. Rev. **37**, 843 (1931).
[19] de Hemptinne, Wouters and Fayt, Bull. Sci. Acad. Roy. Belg. **19**, 318 (1933).
[20] *Handbuch und Jahrbuch der Chem. Phys.* (Leipzig, 1934), Band 9, Teil II, p. 390.
[21] This is equivalent to calling the symmetry coordinates described above for $\eta(\pi)$ and $\eta(\sigma)$ normal coordinates.

TABLE VII. *Correlation of fundamental frequencies of $SiCl_4$, $HSiCl_3$, $BrSiCl_3$ and Si_2Cl_6.*

$SiCl_4$ (T_d)	$HSiCl_3$ (C_{3v})	$BrSiCl_3$	Si_2Cl_6	(D_3, D_{3d})(?)
A 425 (10)	489 (7)	362 (v. str.)	354 (10)	A_1, A_{1g}
	250 (3) **A_1**	123	124 (8)	
		or	or	
608 (2)	2258 (8)	325	132 (5)	
T_2 220 (5)				
	799 (1)	201		
E 150 (5)	587 (1) **E**	410	590 (3)	**E**, E_g
	179 (4)	183 (str.)	212 (4)	

TABLE VIII. *Assignment of the Raman frequencies of Si_2Cl_6, assuming internal rotation.*[25]

$\Delta\nu$ cm^{-1}	Intensity	Assignment (See Fig. 2)
	Fundamentals	
354	10	$\nu_s(\pi)$
132 (or 124)	5 (or 8)	$\delta_s(\pi)$
179	0.4	η (?)
590	3	$\nu(\sigma)$
212	4	$\delta(\sigma)$
124 (or 132)	8 (or 5)	τ (?)
	Combinations and overtones	
421	$<<<1$	$2\delta(\sigma)$
487	$<<<1$	$\delta_s(\pi)+\nu_s(\pi)$
565	$<<1$	$\delta(\sigma)+\nu_s(\pi)$
706	$<<<1$	$2\nu_s(\pi)$
377	$<<1$	$124\ cm^{-1}+252\ cm^{-1}$ (?)
387	$<<1$	$132\ cm^{-1}+252\ cm^{-1}$ (?)
460	$<<<1$	$\delta(\sigma)+252\ cm^{-1}$ (?)
625	2	$\nu_s(\pi)+252\ cm^{-1}$ or (?) in accidental deg. with $\nu(\sigma)$ (?)

force constant is that calculated above from Si_2H_6, its frequency should be 201 cm^{-1}. (A similar calculation using C_2H_6[13] and C_2Cl_6[22] data predicts a frequency of 354 cm^{-1} for η of C_2Cl_6, and a line belonging to the completely symmetric IR is observed at 342 cm^{-1}.) Since the frequency corresponding to the η vibration in C_2H_6, Si_2H_6 and C_2Cl_6 in each case appears with appreciable intensity in its Raman spectrum, we should expect it to appear also in Si_2Cl_6. Therefore it seems to us more likely that 179 cm^{-1} is η rather than $\delta_a(\sigma)$.

The observed line at $\Delta\nu=625$ cm^{-1} appears with considerable intensity, yet it does not seem possible to us that it is due to a fundamental frequency. Its polarization ratio shows that it is not due to a degenerate fundamental frequency. Reference to Table IV shows that only $\nu_s(\pi)$, $\delta_s(\pi)$, η, and ω_i are permitted to be Raman active among the nondegenerate fundamentals in any of the models considered. Of these only $\nu_s(\pi)$ would be expected to be of relatively high frequency, but 354 cm^{-1} is definitely assigned as $\nu_s(\pi)$. $\Delta\nu=625$ cm^{-1} must therefore be due to a combination or overtone. Its intensity then indicates that it probably corresponds to a level in accidental degeneracy with 590 cm^{-1}. Since 590 cm^{-1} shows a ρ value of 6/7 and 625 cm^{-1} a ρ value of <0.5, and since interaction between two levels may occur only if their wave functions belong to representations including the same IR, then the wave function corresponding to 625 cm^{-1} must belong to a representation including both $\mathbf{A_1}$ and **E** of the appropriate point group. Of the first overtones or one-one combinations for each of the symmetries $\mathbf{D_3}$, $\mathbf{D_{3d}}$ and $\mathbf{D_{3h}}$ only an overtone of a degenerate fundamental or a combination of two degenerate fundamentals belonging to the same IR satisfy this requirement.[23] If this interpretation is correct[24] either $2\delta(\sigma)$, 2τ or $\delta(\sigma)+\tau$ should be approximately 608 cm^{-1}, although this is not the case for the present proposed assignment. It is interesting to note that combination of 354 cm^{-1} with the hypothetical 252 cm^{-1} frequency gives a level at approximately 608 cm^{-1}, but this level would not satisfy the requirements just mentioned.

The above analysis does not permit a definite answer to the question of internal rotation in Si_2Cl_6 at room temperature, but affords some evidence for its existence. In Table VIII is shown a tentative assignment of the observed lines under the assumption that free rotation does exist.[25]

In conclusion we wish to thank Professor E. B. Wilson, Jr. and Dr. J. B. Howard for valuable criticism and discussion.

Note added in proof. Very recently Kemp and Pitzer (J. Chem. Phys. **4**, 749 (1936)) have presented evidence for the existence of a potential barrier of about 3150 cal./mole between the $\mathbf{D_{3d}}$ and $\mathbf{D_{3h}}$ configurations in ethane. Since the Si—Si distance (2.34A) in Si_2H_6 and Si_2Cl_6 is considerably greater than the C—C distance (1.52A) in ethane, their conclusions would not appear to exclude the possibility of internal rotation in Si_2H_6 and Si_2Cl_6.

[22] Heidenreich, Zeits. f. Physik **97**, 277 (1935).

[23] See Tisza, Zeits. f. Physik **82**, 48 (1933).

[24] In this case the numerical agreement between 587 cm^{-1} of $HSiCl_3$ and 590 cm^{-1} of Si_2Cl_6 loses some of its significance as evidence for free rotation.

[25] If instead a rigid (reference 17) $\mathbf{D_{3d}}$, or even $\mathbf{D_{3h}}$, structure exists, subscripts *s* on the degenerate frequency designations in Table VIII would be the only change necessary for the appropriate new tentative assignments.

Photochemical Reduction with X-Rays and Effects of Addition Agents

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Ceric sulfate solution was reduced by exposure to x-radiation. In order to follow this reaction a very accurate method was developed for the determination of ceric sulfate in dilute solutions by the use of orthophenanthroline indicator. The amount of reduction of ceric sulfate by x-rays was found to be practically independent of concentration. Reduction was shown to be directly proportional to time of exposure up to 50 percent and slightly less efficient beyond that point. Silver perchlorate and silver nitrate decreased the amount of reduction of ceric sulfate by x-rays. Mercuric nitrate and acetic acid increased the amount of reduction caused by x-rays. Curves are also presented to show the effect of changing the concentration of these addition agents. Indications are that the mercuric nitrate was truly a catalyst to the reduction of ceric sulfate by x-rays and that the acetic acid increased the amount of reduction by direct action on the ceric sulfate under the influence of x-rays. Perchloric and nitric acids increased the reduction of ceric sulfate appreciably but not to as great an extent as did $Hg(NO_3)_2$. Sodium nitrate, perchlorate and sulfate showed no effect. Various organic substances were tried and found to increase the reduction by varying amounts. Experiments were carried out with various combinations of the catalysts and inhibitors to determine their relative efficiencies. The reduction of potassium permanganate by x-rays proceeded to manganese dioxide for low acid concentrations and to manganous ion at higher acidity. The reaction was greater than for ceric sulfate but not as nearly proportional to dosage. The effect of addition agents was similar to that for ceric sulfate. X-rays did not produce the same reaction in solutions of uranyl sulfate-oxalic acid as does ultraviolet radiation. Solutions of potassium iodate were reduced by x-rays but to a less degree than ceric sulfate or potassium permanganate. Hydrogen peroxide was formed in samples during radiation but did not effect the potassium iodate. Solutions of potassium bromate were not reduced by x-rays but even larger amounts of hydrogen peroxide were formed. Calculations were made for: ions reduced per r unit absorbed, r units necessary for reduction of one equivalent, ions reduced per ion pair formed by x-rays, and calories of absorbed energy necessary for reduction of one equivalent, by two independent methods. A mechanism was proposed for the formation of hydrogen peroxide by x-rays in the presence of dissolved oxygen.

PHOTOCHEMICAL reduction of inorganic compounds by x-rays is an interesting field of investigation which already has received some attention. Chamberlain[1] has reported the reduction of potassium permanganate and potassium iodate by x-rays. These results were only qualitative. Clark and Pickett[2] made the same observation and did quantitative work on the photolysis of potassium nitrate and potassium iodide by x-rays. Fricke and Brownscombe,[3] and Fricke and Washburn[4] have noted the reduction of potassium dichromate by x-rays and attributed it to the formation of hydrogen peroxide. These workers have also observed large effects of impurities in the irradiated solution.

The formation and decomposition of hydrogen peroxide by x-rays have been the subject of much investigation because of the possibility of its influence on any x-ray photochemical reaction in aqueous medium. Glocker and Risse[5, 6] studied the effect of wave-length and concentration upon the decomposition of hydrogen peroxide. Risse reported the formation of hydrogen peroxide by x-rays in water containing dissolved oxygen. Fricke[7] and Brownscombe[8] confirmed his report and showed that no hydrogen peroxide was formed in pure air-free water.

The purpose of the present work was to contribute to the knowledge of the quantitative aspects of reductions by x-rays of familiar inorganic reagents in dilute aqueous solution and the catalytic or inhibitory effects of various substances added voluntarily to these solutions.

EXPERIMENTAL

The x-ray tube used for the irradiation of solutions during this investigation was one designed by the authors and constructed in the machine shop at the University of Illinois. It was designed with a metal body for self-protection from stray radiation, a water-cooled copper or tungsten anode to allow a high tube current, and a special aluminum-beryllium alloy window for the efficient transmission of x-rays but not light or heat. A complete description of this tube will appear elsewhere.

Determination of intensity of radiation

Intensity measurements were taken with a Victoreen R meter and corrections made for temperature and atmospheric pressure to give values in terms of the internationally accepted *r* unit[9] of x-radiation. The effective wave-length of x-rays emitted from both copper and tungsten targets operating at 55 kilovolts was determined by the method of Duane, Hudson and Sterling[10] involving the determination of percent transmission by a 2 mm aluminum plate. Values of 0.62A for the copper target and 0.60A for the tungsten target were obtained. The general experimental procedure for irradiation was to expose 10 cc of the solution in a 50 cc beaker at a distance of 15 or 20 cm from the focal spot, with the tube operating at 55 kilovolts. Some exposures were made with a tube current of 20 and others with 30 milliamperes.

Absorption coefficients calculated for water for the two effective wave-lengths used ($\mu=0.826$ for $\lambda=0.62$A and $\mu=0.746$ for $\lambda=0.60$A) agree satisfactorily with interpolations from a series given by Glocker and Risse.[5]

Method for estimation of ceric sulfate

Since it was desired to determine quantitatively the amount of ceric sulfate reduced by reasonably short exposures to x-rays a very precise method of titration had to be developed. Potentiometric titration with 0.001 *N* ferrous sulfate was tried but found to be only partially satisfactory. Since orthophenanthroline[11] has been widely used as an oxidation-reduction indicator in solutions of ordinary concentration and found to give a very sharp end point, it was thought probable that application might be made of this indicator even in dilute solutions. The following procedure has been used and found very satisfactory: the orthophenanthroline ferrous complex was made up to one-fifth the usual concentration (0.005 *M* instead of 0.025 *M*) and one drop of the solution used for a 10 cc sample. Sufficient sulfuric acid was added to the sample to make it approximately 1 *N* and titration carried out with 0.001 *N* ferrous sulfate. Under these conditions the end point was detected as the first appearance of a permanent pink color in contrast to the colorless solution before the end point. This change was noticeable with 0.01 cc of 0.001 *N* ferrous sulfate and very pronounced with 0.02 cc, particularly when illuminated with a strong light on a white table and with a white background. It is evident that the indicator correction was very large since the indicator contained 0.005 *N* Fe^{++}. However, nonirradiated controls were always titrated at the same time as the irradiated samples so the difference due to x-radiation did not depend on indicator correction as long as it was kept constant. The proper correction was made when direct comparison of the two solutions was necessary.

The procedure finally adopted for the preparation of these ceric sulfate solutions was to recrystallize the ceric ammonium sulfate until a very pure product was assured; then it was ignited in a muffle furnace at 900 to 1000°C for eighteen hours to convert it to the oxide. Decomposition took place at a lower temperature but also some reduction was caused by the ammonia liberated. The prolonged heating in the presence of oxygen of the air reoxidized the product to ceric oxide. This oxide was then treated with a small amount of concentrated sulfuric acid (9 parts H_2SO_4 to 1 part H_2O) to convert it to the sulfate. The purified ceric sulfate was finally dissolved in water and diluted to convenient stock concentration. The solutions were always strongly acidic with the excess sulfuric acid necessary to react with the oxide.

These solutions, as well as all others used for irradiation in this investigation, were prepared from "conductivity" water redistilled from alkaline permanganate.

Reduction of ceric sulfate solutions by x-radiation

Experiments showed that the amount of reduction was practically independent of the concentration of ceric sulfate for dilute solutions. This is consistent with most photochemical effects of x-rays. The amount of reduction did increase slightly for more concentrated solutions of ceric sulfate (above 0.001 *M*).

Since the ceric sulfate stock solution was quite acidic with sulfuric acid the dependence of reduction upon acid concentration was determined. Increasing the sulfuric acid concentration from 0.05 *N* to 1.2 *N* decreased the amount of reduc-

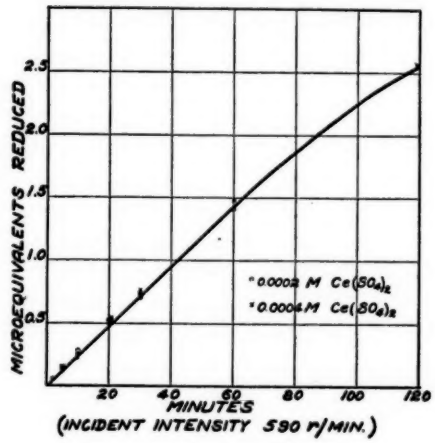

FIG. 1.

tion by a given dosage of x-rays in 0.0002 *M* $Ce(SO_4)_2$ by approximately 10 percent.

The next step was to determine the function of reduction with time of radiation. This series of experiments was carried out with 10 cc samples of 0.0002 *M* and 0.0004 *M* $Ce(SO_4)_2$ in 0.1 *N* H_2SO_4. Fig. 1 is a curve showing the microequivalents reduced against minutes irradiation (20 milliamperes, 590 *r*/min. incident intensity). It can be seen that the amount of reduction is very nearly proportional to dosage up to 50 percent. The sixty minute value for 0.0002 *M* $Ce(SO_4)_2$ which corresponds to approximately 75 percent reduction is somewhat low indicating that the rate of reaction has decreased slightly. The one hundred and twenty minute value for 0.0004 *M* $Ce(SO_4)_2$ shows a similar behavior.

Effect of added substances upon reduction of ceric sulfate

During the investigation of the effect of various dosages upon amount of reduction one sample was exposed after a drop of the orthophenanthroline indicator had been added. The amount of reduction in that sample was almost double that of samples given the same irradiation without the indicator present. Further experiments with Fe^{++} added to the concentration present in the indicator failed to cause any irregularity in results. The increased reduction, then, must have been due to the organic part of the indicator.

It was thought of interest to determine what effect small amounts of Ag^+ might have on the amount of the reduction of ceric sulfate by

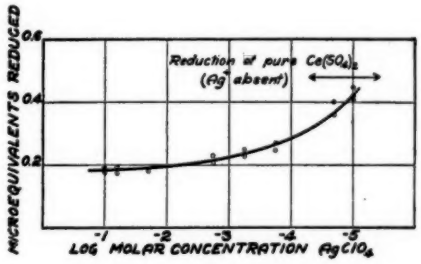

FIG. 2.

x-rays. Inasmuch as the Ag^+ would cause the solution to absorb a larger percentage of x-rays it might be predicted that a greater amount of reaction would take place. On the contrary Ag^+ was actually found to be a very efficient inhibitor for the reaction. Fig. 2 is a curve showing amount of reduction in 10 cc of 0.0002 *M* $Ce(SO_4)_2$, 0.1 *N* H_2SO_4 against the log of the concentrations of $AgClO_4$ present. $AgNO_3$ was also used and the values agree within experimental error with those for $AgClO_4$. These values were taken with copper target radiation with the tube operating at 55 peak and 30 milliamperes for fifteen minute exposures. The solutions were placed 15 cm from the focal spot and the incident intensity of radiation was 775 *r*/min. From the curve it is seen that even 10^{-5} *M* $AgClO_4$ has a definite inhibitory effect upon the course of the reduction and 0.1 *M* $AgClO_4$ decreases the amount of reduction to approximately one-third of its ordinary amount.

Since silver salts were found to have such a marked effect, other salts of heavy metals were tried to see if they might behave in a similar way. However, mercuric nitrate was found to show a very strong behavior in the *opposite* direction, that is, increasing the amount of reduction of

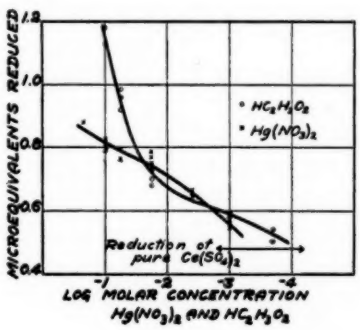

FIG. 3.

TABLE I

ADDITION AGENT (CONCN. APPROX. 0.02 *M*)	MICROEQUIVALENTS $Ce(SO_4)_2$ REDUCED
None	0.48
Ethyl alcohol	.61
Diethyl ether	.71
Dibutyl ether	.73
Acetone	.51
Carbon tetrachloride	.57
Ethyl acetate	.51
Dioxane	.55
Benzene	1.12

ceric sulfate. One curve of Fig. 3 shows the amount of reduction in 0.0002 *M* $Ce(SO_4)_2$, 0.1 *N* H_2SO_4 plotted against the logarithm of molar concentration of $Hg(NO_3)_2$ for the same conditions of irradiation as used for sample represented by Fig. 2. A curve is also shown for acetic acid which has been found to have an effect similar to that of mercuric nitrate. It is well to mention again that the values given for amount of reduction are differences in amount of standard $FeSO_4$ necessary to titrate the irradiated sample and a similar nonirradiated control. The values recorded are then due to the action of x-rays and independent of any direct action beween ceric sulfate and the added substance.

The effects of $HClO_4$ and HNO_3 on the reduction of $Ce(SO_4)_2$ by x-rays were also determined. In each case the amount of reduction was increased but not to as great an extent as for $HC_2H_3O_2$ and $Hg(NO_3)_2$. Whereas, 0.48 microequivalents of 0.0002 *M* $Ce(SO_4)_2$, 0.1 *N* H_2SO_4 were reduced under conditions stated above, 0.1 *M* $HClO_4$ increased this value to 0.57 microequivalents and 0.1 *M* HNO_3 to 0.59 microequivalents. Bismuth nitrate was also found to increase the amount of reduction considerably but the separation of bismuthyl sulfate prevented an exact quantitative estimate under the same conditions as used for the other substances. On the other hand, 0.05 *M* $CuSO_4$ acted more like $AgClO_4$ and decreased the amount of reduction to 0.38 microequivalents. $NaNO_3$, $NaClO_4$, and Na_2SO_4 were also tried but found to give no appreciable effect.

Various organic substances were also tried. Some were found to increase the amount of reduction very markedly and others to a lesser extent. Table I shows the substances studied and gives the microequivalents reduced under the same conditions of irradiation as preceding experiments.

Since both catalytic and inhibitory effects were noticed for single substances added to ceric sulfate solutions, it was of interest to see if these behaviors would be additive when two substances were present in the same solution. Experiments with 0.06 *M* $Hg(NO_3)_2$, 0.06 *M* $HC_2H_3O_2$, and 0.02 *M* $Hg(NO_3)_2$, 0.02 *M* $HC_2H_3O_2$ indicated that the reduction was increased to a greater extent than by either single substance but not as much as to be directly additive. The next combination tried was one catalyst and one inhibitor such as $HC_2H_3O_2$ and $AgClO_4$, or $Hg(NO_3)_2$ and $AgClO_4$. Curves in Fig. 4 show the amount of reduction for a constant concentration of the catalysts (0.02 *M* $HC_2H_3O_2$; 0.06 *M* $Hg(NO_3)_2$) in 0.0002 *M* $Ce(SO_4)_2$, 0.1 *N* H_2SO_4 for varying concentrations of the inhibitor $AgClO_4$. In both cases $AgClO_4$ was found to be much more efficient as an inhibitor than the other substance as a catalyst. This is easily seen on the graph since the points where the curves intersect the line drawn to indicate reduction in pure $Ce(SO_4)_2$ represent the condition of balance between catalyst and inhibitor. Thus, 0.0001 *M* $AgClO_4$ ($\log = -4$) neutralizes the effect of 0.02 *M* $HC_2H_3O_2$ and 0.002 *M* $AgClO_4$ ($\log = -2.7$) corresponds to 0.06 *M* $Hg(NO_3)_2$.

Experiments with potassium permanganate and added substances

The reduction of potassium permanganate has been noted by other investigators; Chamberlain[1] reported reduction to Mn^{++} and Clark and Pickett[2] reported the formation of MnO_2. These results were only qualitative, probably because a satisfactory method for estimation of dilute solutions of potassium permanganate was not available. Preliminary qualitative investigation confirmed the observations cited and showed that MnO_2 was formed by irradiation of solutions of potassium permanganate less than 0.1 *N* with respect to H_2SO_4. Solutions of higher acidity (1.0 *N* H_2SO_4) were reduced directly to Mn^{++} and varying amounts of MnO_2 and Mn^{++} were formed for intermediate concentrations.

Quantitative determination of reduction was found possible by a procedure similar to that used for ceric sulfate. However, the orthophenan-

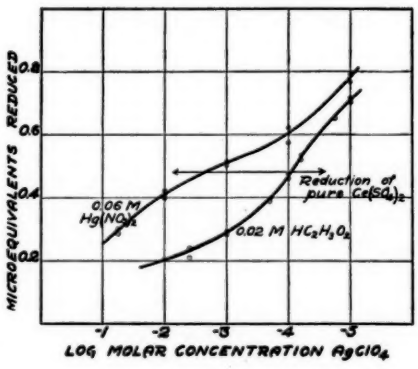

FIG. 4.

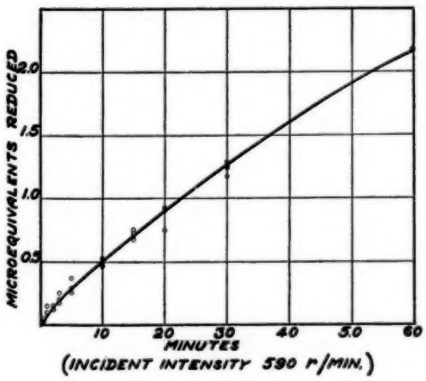

FIG. 5.

throline end point with 0.001 N $FeSO_4$ was neither as sharp nor as permanent as for ceric sulfate and a titration error of approximately ± 0.03 cc was thus introduced.

A study of the amount of reduction of $KMnO_4$ by different dosages of x-rays was carried out in a manner similar to that for $Ce(SO_4)_2$. Ten cubic centimeter samples of 0.0004 N $KMnO_4$, 1.0 N H_2SO_4 were used. Fig. 5 is a curve showing microequivalents reduction plotted against minutes radiation, 20 cm from tungsten target, operating at 55 peak and 20 milliamperes (incident intensity 590 r/min.).

From the curve it is seen that the relation between reduction of potassium permanganate and dosage is not so nearly linear as was the case for ceric sulfate. The curve shows a sharp rise for the first few minutes; this may indicate that x-rays catalyze the reduction of $KMnO_4$ by slight traces of organic materials remaining in the solution in spite of precautions taken to prevent such contamination. This is further borne out by the fact that slight amounts of added organic substances were found to increase the reduction to a great extent. Orthophenanthroline as dilute as 0.00002 M increased the reduction for a ten minute exposure to three times its normal amount.

Mercuric nitrate and acetic acid increased the reduction of potassium permanganate in the same manner as for ceric sulfate. Whereas, approximately 0.49 microequivalents were reduced by a ten minute exposure of 0.0004 M $KMnO_4$, 1 N H_2SO_4 solution, the presence of 0.05rM $Hg(NO_3)_2$ or 0.05 M $HC_2H_3O_2$ augmented this value to 1.09 and 1.12, respectively.

The reduction of $KMnO_4$ was inhibited by $AgClO_4$, and $AgNO_3$ as would be expected by comparison with their behavior with $Ce(SO_4)_2$. This reduction was decreased from 0.49 microequivalents to 0.18 in the presence of 0.05 M $AgClO_4$ and to 0.22 for 0.05 M $AgNO_3$.

Experiments with uranyl sulfate-oxalic acid solution

Uranyl sulfate-oxalic acid solutions have been widely used as an actinometer for sunlight or ultraviolet radiation.[12, 13] The procedure usually employed is to titrate radiated samples and controls with standard potassium permanganate to a faint pink color, the difference in amount of permanganate being a measure of the amount of oxidation of $H_2C_2O_4$ by radiation, catalyzed by uranyl sulfate. Since the reaction is quite large with ultraviolet, it was thought that some reaction might be noted by x-rays.

A solution of 0.005 M $H_2C_2O_4$, 0.002 M UO_2SO_4 was prepared and samples exposed to x-radiation. No reaction could be detected, so again it was found that behavior with ultraviolet was not safe evidence for prediction of the action of x-rays. Further experiments using a very large dosage of x-rays (17 cm, Cu target, 30 milliamperes, 55 kv, 2 hours) even showed that approximately 0.10 cc more 0.01 N $KMnO_4$ was necessary for the titration of the radiated samples than for the controls. However, the titration reaction was very slow near the end point for the radiated samples; this was probably due to the fact that a small amount of hydrogen peroxide had been formed by x-radiation and was re-

sponsible for the extra amount of $KMnO_4$ necessary.

Experiments with potassium iodate and potassium bromate

Since this investigation was primarily concerned with reduction effects of x-rays, it was desirable to examine the effect upon potassium iodate and potassium bromate. Stock solutions were carefully prepared from reagent quality chemicals and redistilled water. Solutions for exposure to x-rays were diluted to 0.0006 *N* and enough sulfuric acid added to make the solutions 0.1 *N*. Ten cubic centimeter samples were placed 15 cm from the copper target tube operated at 55 peak and 30 milliamperes (incident intensity 720 *r*/min.).

The samples were examined by adding excess potassium iodide and titrating almost to the disappearance of the liberated iodine with 0.001 *N* $Na_2S_2O_3$. Starch was then added and the titration continued to the disappearance of the blue color. This end point is capable of detection to ± 0.01 cc of 0.001 *N* $Na_2S_2O_3$. It was necessary to add more sulfuric acid for the titration of the bromate samples.

Preliminary experiments with potassium iodate showed that reduction did take place but to a less extent than for ceric sulfate and potassium permanganate. The time of exposure was increased to one hour and several measurements taken on the amount of reduction for that time. An average of 0.55 microequivalents was reduced. Titration of these samples seemed to proceed to a sharp and stable end point but upon standing thirty minutes or longer the radiated samples become blue again while the controls remained unchanged. Further titration with sodium thiosulfate solution after two hours gave another sharp end point which was stable over a long period except as atmospheric oxidation caused a gradual change for the acidity used (0.1 *N* H_2SO_4). Repeated experiments revealed that the second titration of the radiated samples depended on time of radiation in the same manner as the reduction noted by the first titration. This second titration averaged 0.42 microequivalents for one hour exposures.

TABLE II.

Samples 10 cc, 0.0006 *N* KIO_3, 0.1 *N* H_2SO_4	First Titration cc 0.001 *N* $Na_2S_2O_3$	Second Titration cc 0.001 *N* $Na_2S_2O_3$
Controls	5.91	0.02
	5.93	.02
Radiated one hour	5.35	.45
	5.38	.43
0.42 microequiv. H_2O_2 added (not radiated)	5.92	.44
	5.94	.45

Since hydrogen peroxide might have been formed in the radiated samples the next procedure was to see if hydrogen peroxide added to the control samples would cause them to behave in the same manner as those that had been radiated. This was at first thought doubtful because the H_2O_2 might be oxidized by the KIO_3 or at least be destroyed during the first titration. However, a series of samples was prepared and the results are indicated in Table II.

It is noted that H_2O_2 did not affect the KIO_3 and did not disturb the titration since the controls necessitated the same amount of $Na_2S_2O_3$ as did those containing H_2O_2. There is a difference of approximately 0.54 microequivalents between the controls and radiated samples corresponding to the reduction by x-rays. After the first titration the solutions were allowed to stand. After ten minutes the radiated samples and those to which H_2O_2 had been added became slightly blue due to the slow liberation of I_2 as the H_2O_2 reacted with HI formed by previous addition of excess KI to the 0.1 *N* H_2SO_4. The blue color continued to develop in both solutions at the same rate proving beyond a doubt that H_2O_2 had been formed in the radiated samples. The second titration was carried out after about two hours and corresponded to the amount of H_2O_2 formed or added. The amount of oxidation of the control samples by air was equivalent to 0.02 cc of $Na_2S_2O_3$. In more concentrated H_2SO_4 solutions the reaction between HI and H_2O_2 was more rapid and consequently the end point for the first titration could not be detected as accurately.

The effect of x-rays upon solutions of potassium bromate was tried in a manner similar to that for potassium iodate but *no* reduction could be detected. However, the second titration showed that even larger amounts of H_2O_2 had been formed than in the case of potassium iodate. Approximately 1.01 microequivalents of H_2O_2

TABLE III.

	$Ce(SO_4)_2$ Reduced (0.1 N H_2SO_4)	$KMnO_4$ Reduced (1.0 N H_2SO_4)	KIO_3 Reduced (0.1 N H_2SO_4)	H_2O_2 Formed (0.1 N H_2SO_4)
"Equivalions" converted per r unit absorbed	4.42×10^{12}	7.45×10^{12}	1.27×10^{12}	2.30×10^{12}
r units absorbed per equivalent converted	1.37×10^{11}	0.81×10^{11}	4.78×10^{11}	2.63×10^{11}
Ions converted per ion pair	2.0	3.7	0.62	1.1
Calories of absorbed energy per equivalent reduced*	379,500	205,135	1,224,193	690,000
Calories electronic energy for conversion of one equivalent†	344,000	204,000	1,095,000	602,000

Note: "Equivalions" equal gram equivalents times 6.06×10^{23}.
* Calculated from ions per ion pair, electron volts per ion pair, and heat equivalence of electron volts.
† Calculated from total heat equivalence of r unit, and total heat dissipated as electronic energy.

were formed for a one hour exposure. Further experiments revealed that about the same amount of H_2O_2 was formed by same radiation of 0.1 N H_2SO_4 (not air-free).

An attempt was made to study the effect of x-rays upon solutions of potassium chlorate but a satisfactory method for the accurate determination of dilute solutions could not be found.

Energy relationships

Ceric ions reduced per r unit.—Values are given in Fig. 1 for amount of reduction of 0.0002 M and 0.0004 M ceric sulfate in 0.1 N H_2SO_4 by tungsten radiation (effective $\lambda=0.60$) for varying periods of exposure. From the straight portion of the curve it can be seen that forty-one minutes were necessary for the reduction of 1.0 microequivalent weight or 6.06×10^{17} ceric ions. Since the incident intensity was 590 r/min. per sq.cm, $590\cdot11.94=7050$ per min. incident radiation on the total surface. Of this amount 47.5 percent was absorbed by 0.1 N H_2SO_4; the absorption due to the small amount of $Ce(SO_4)_2$ present is negligible. From this it is calculated that 137,000 r units were absorbed in forty-one minutes. Therefore, 6.06×10^{17} ions per 137,000 r units or 4.42×10^{12} ions per r unit absorbed were reduced; 1.37×10^{11} r units were necessary for complete reduction of one mole of ceric ions.

By definition one r unit corresponds to an ionization such that a current of 1 e.s.u. flows in 1.0 cc of air under saturation potential. The number of ion pairs in air is therefore:

$$\frac{\text{total energy}}{\text{charge on electron}}=\frac{1}{4.774\times10^{-10}}$$

$$=2.1\times10^{9}\text{ ion pairs/cc}$$

in air and $2.1\times10^{9}\cdot795^{*}=1.7\times10^{12}$ ion pairs per cc per r unit incident radiation on the water surface. These calculations assume a very thin layer of fluid so that the incident intensity is the same on all portions. Since this was not the case for the experimental conditions used, it is necessary to calculate the average incident intensity compared to that at the surface. Using the absorption equation $I=I_0e^{-\mu x}$ and allowing I_0 to be 100 percent, the area under the curve of intensity against depth of solution can be found as $\int^{0}_{.84}100\,e^{-\mu x}dx$. Dividing this value by 0.84 gives an average for all portions of the solution of 73.3 percent of the intensity incident upon the surface. There were, then, 590 r/min.$\cdot0.733\cdot1.7\times10^{12}$ $=7.35\times10^{14}$ ion pairs per cc per min. in the solution under the conditions used. But, one microequivalent (6.06×10^{17} ions) of ceric ions was reduced for a forty-one minute exposure in 10 cc; this gives:

$$\frac{6.06\times10^{17}}{7\,35\times10^{14}\cdot10\cdot41}=2.01\text{ ions reduced per ion pair.}$$

Energy of reduction in calories per equivalent of ceric ions.—This calculation comes out directly from the ions reduced per ion pair (2.01), the energy in electron volts to produce an ion pair (33 volts) and the heat equivalence per mole of the electron volt (23,000). The result is 379,000 calories per mole of ceric sulfate. By an entirely independent method based on the best data available on total heat equivalence of the r unit (148 ergs per r unit at the given wave-length) and the proportion of total heat dissipated as electronic energy (0.71), the value 344,000 calories is

* The best value correlating the number of ion pairs in water and in air in terms of density difference.

obtained. A check within 10 percent for these two different calculations would seem to be highly satisfactory.

Discussion of results

Table III shows the results for ceric sulfate in tabular form and also values for $KMnO_4$, KIO_3, and H_2O_2 as computed from similar calculations. It should be noted that all values are in terms of oxidation-reduction equivalents instead of moles. The values would be the same for ceric ion but would differ by a factor of 5 for $KMnO_4$, 6 for KIO_3 and 2 for H_2O_2. This method of tabulation allows direct comparison of the oxidation-reduction change brought about by x-rays in the different substances. An appropriate term, "equivalons," has been used to indicate a single "equivalent" ion and bears the same relation to gram equivalent as does the molecule to the gram mole. The values given for $Ce(SO_4)_2$, $KMnO_4$, and KIO_3 are for amount of reduction by x-rays and the values for H_2O_2 designate the amount formed in 0.1 N H_2SO_4 in the presence of dissolved oxygen.

The reduction of ceric sulfate and potassium permanganate by x-rays is undoubtedly a complicated process involving both the formation of H_2O_2 and direct reduction by activated water. The importance of the activated water molecule in x-ray photochemistry has been repeatedly shown by Fricke[14] and co-workers. This accounts for the fact that most effects of x-rays are independent of concentration of reactant.

Since all solutions irradiated were open to the air, dissolved oxygen was present in solution and the production of H_2O_2 by x-rays proceeded according to the over-all equation:

$$2H_2O+O_2=2H_2O_2. \qquad (1)$$

The mechanism for this reaction has never been established although various ones have been suggested. Risse[15] postulated two mechanisms for the decomposition of H_2O by x-rays and subsequent formation of H_2O_2. These mechanisms with added values for heats of reaction (H=heat evolved) as calculated from data given by *International Critical Tables* and Lewis and von Elbe[16] are as follows:

$2(H_2O\ (act.)=H+OH)$	$\Delta H=-228{,}800$ cal.
$2OH\ \ =H_2O_2$	$\Delta H=\ \ 34{,}100$ cal.
$2H+O_2\ \ =H_2O_2$	$\Delta H=\ 147{,}700$ cal.
Total $2H_2O+O_2=2H_2O_2$	$\Delta H=-\ 47{,}000$ cal.
or $2(H_2O\ (act.)=2H+O)$	$\Delta H=-501{,}400$ cal.
$2O\ \ =O_2$	$\Delta H=\ 163{,}000$ cal.
$2(2H+O_2\ \ =H_2O_2)$	$\Delta H=\ 291{,}400$ cal.
Total $2H_2O+O_2=2H_2O_2$	$\Delta H=-\ 47{,}000$ cal.

These mechanisms require very large activation energies and also have the disadvantage of requiring collision between two groups that could not be present in large amounts, such as 2 OH's in the first case and 2 O's in the second. In view of these facts a more logical mechanism would seem to be:

$H_2O\ (act.)+O_2=H_2O_2+O$	$\Delta H=-105{,}000$ cal.
$H_2O+O\ \ =H_2O_2$	$\Delta H=\ \ 58{,}000$ cal.
Total $2H_2O+O_2=2H_2O_2$	$\Delta H=-\ 47{,}000$ cal.

This is also consistent with the fact that the formation of H_2O_2 has not been observed in pure (O_2 free) water. The activation energy involved is moderate and the water molecule itself is a reactant in each step.

Since hydrogen peroxide reduces ceric sulfate in acid solution, any H_2O_2 formed by x-rays reacted immediately, according to:

$$2Ce^{++++}+H_2O_2=2Ce^{+++}+2H^++O_2. \qquad (2)$$

However, it can be seen from Table III that such a reaction could not account for the amount of reduction noted. Therefore, an additional direct reaction must have been caused by other activated water molecules. The actual mechanism of reduction was probably a direct combination with secondary electrons liberated from water molecules by x-ray photons, but the over-all reaction would be:

$$2Ce^{++++}+H_2O\ (act.)=2Ce^{+++}+2H^++1/2O_2. \qquad (3)$$

It is recognized, of course, that the production of H_2O_2 is determined in cerium-free solutions and that in this case part of the H_2O_2 produced is again decomposed by x-rays.[17] From the data of Fricke under the conditions of the experiment, nearly half of the H_2O_2 would be decomposed. Hence, the reduction of ceric ions can more nearly

be accounted for by allowance for the initial production of H_2O_2. Further proof for the type of direct reaction mentioned above is furnished by the fact that KIO_3 solutions were reduced by x-rays but not affected by H_2O_2 added or formed by irradiation. This is also consistent with the smaller amount of reduction noted for KIO_3 than for $Ce(SO_4)_2$. $KMnO_4$ was reduced to an even greater extent than $Ce(SO_4)_2$, probably due to a higher efficiency of the direct reduction by activated water or secondary electrons.

From Eq. (3) it is to be noted that the liberation of oxygen accompanies the process of reduction in solutions irradiated by x-rays. Therefore, conditions for formation of hydrogen peroxide are soon established even if irradiation is executed in air free solutions in closed containers. A few exposures with freshly boiled solutions showed that the reaction proceeded a little more slowly at the beginning.

The reduction of IO_3^- apparently proceeded only to the stage of IO^- because no free I_2 was detected by the addition of starch for the titration until excess KI was added. The over-all equation would be:

$$IO_3^- = H_2O\ (\text{act.}) = IO^- + O_2 + H_2O. \qquad (4)$$

It is impossible to state whether the O_2 liberated came from H_2O or IO_3^-. The answer may be that one O came from each.

As yet, no logical explanation has been found to interpret the fact that BrO_3^- was not reduced by x-rays in a manner similar to that for IO_3^-. It is even more puzzling in view of the fact that the reaction, $BrO_3^- = BrO^- + O_2$, is slightly exothermic while the similar one for IO_3^- is endothermic.

The decrease in amount of reduction of ceric sulfate by x-rays in the presence of Ag^+ indicates that the heavy silver ion absorbed the activation energy from H_2O before it was effective in producing reduction. On the other hand, Hg^{++} seemed to act as an efficient acceptor for the activation energy from the water or for secondary electrons and brought about increased reduction of ceric sulfate by intermediate reduction to Hg_2^{++} and reoxidation by Ce^{++++}.

Acetic acid also increased the amount of reduction of ceric sulfate by x-rays, but as pointed out previously, the difference in the shape of the curves of reduction versus concentration of $Hg(NO_3)_2$ and $HC_2H_3O_2$ (Fig. 3) would seem to indicate that x-rays produced the necessary activation energy to promote direct reaction between the acetic acid and ceric sulfate. Since no method was available for the accurate determination of the amount of acetic acid remaining, this could not be proven definitely.

Bibliography

[1] Chamberlain, Phys. Rev. **26**, 525 (1925).
[2] Clark and Pickett, J. Am. Chem. Soc. **52**, 465–479 (1930)
[3] Fricke and Brownscombe, J. Am. Chem. Soc. **55**, 2358–2363 (1933).
[4] Fricke and Washburn, Phys. Rev. **40**, 1033 (1932).
[5] Glocker and Risse, Zeits. f. Physik **48**, 845–851 (1928).
[6] Risse, Zeits. f. physik. Chemie **A140**, 133–157 (1929).
[7] Fricke, J. Chem. Phys. **2**, 349 (1934).
[8] Fricke and Brownscombe, Phys. Rev. **44**, 240 (1933).
[9] Clark, *Applied X-Rays* (McGraw-Hill, 1932), p. 163.
[10] Duane, Hudson and Sterling, Am. J. Roentgenol. Radium Therapy **20**, 241–245 (1928).
[11] Smith, *Ortho-Phenanthroline* (The G. Frederick Smith Chemical Co., Columbus, Ohio).
[12] Leighton and Forbes, J. Am. Chem. Soc. **52**, 3139–3152 (1930).
[13] Mayerson, Am. J. Hyg. **22**, 106–136 (1935).
[14] Fricke, Sym. Quant. Biol. **3**, 55–65 (1935).
[15] Risse, Strahlentherapie **34**, 578–581 (1929).
[16] Lewis and von Elbe, J. Chem. Phys. **3**, 63 (1935).
[17] Fricke, J. Chem. Phys. **3**, 364 (1935).

The Effect of Foreign Molecules on the Absorption Coefficient of Oxygen in the Schumann Region

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The absorption coefficient of oxygen in the continuous band having a maximum at 1450A is not altered by the addition of 80 percent nitrogen at pressures less than 15 mm of mercury, the range covered by these experiments. The conclusion is drawn that, at least at low pressures, the absorption of oxygen in the Schumann region is not effected by collisions with foreign molecules.

ABSORPTION of ultraviolet light by oxygen in a band having a maximum near 1450A has been used as a means of inducing photochemical reactions involving oxygen. According to Herzberg,[1] the absorption of a light quantum of wave-length shorter than about 1800A results in the production of a neutral and an excited oxygen atom. Since the interpretation of some of these photochemical studies depends on the assumption that the absorption of oxygen in this band is not altered by the presence of foreign molecules, an investigation of the validity of this assumption seemed advisable.

The apparatus for measuring the absorption of oxygen consisted of a hydrogen discharge tube, a vacuum spectrograph and two cells of length 2.27 and 4.75 cm equipped with lithium fluoride windows. The cells were introduced, one at a time, between the light source and the slit of the spectrograph. The absorption of the gas was measured quantitatively by comparing the intensity of the light passing through the tube when evacuated to a pressure less than 5×10^{-5} mm of mercury with the intensity when gas was introduced at a known pressure. Further details of the method of photographic photometry used in these experiments have been given in a previous publication.[2]

A mixture of 20 percent oxygen and 80 percent nitrogen was selected for investigation because this combination was used as a standard by G. B. Kistiakowsky[3] in studying the reaction of oxygen and hydrogen induced by absorption of extreme ultraviolet light. Tank nitrogen when purified by passing over hot copper and dried with phosphorous pentoxide was completely transparent in the wave-length region covered in this investigation provided the pressure was lower than 10 cm in the longer cell. Since the pressure was kept below this value for all of the measurements, the absorption of the nitrogen may be neglected. Furthermore, since Warburg[4] has found that the yield of ozone per quantum of absorbed ultraviolet light is not changed by the addition of nitrogen, the nitrogen may be considered as an inert gas.

Because the oxygen disappeared slowly during prolonged exposure to ultraviolet light, it was necessary to keep the gas flowing through the cell. The flow was sufficient to completely change the gas in the absorption tube five times a minute.

Since there is negligible change in reflection of the light at the surface of the absorption tube when the pressure of the gas is altered a few millimeters, the intensity of the light, **I**, transmitted by the gas column may be expressed in the following form:

$$I = I_0 e^{-apd},$$

where $\mathbf{I}_0$ is the intensity through the cell when highly evacuated, **a** is the absorption coefficient per unit length per unit pressure, **p** is the pressure, and **d** is the length of the gas column.

This equation shows that a plot of $\log_e I_0/I$ against **pd** should be a straight line if the absorption coefficient of oxygen is not altered by an increase in pressure of the gas. Fig. 1 shows such a plot for three wave-lengths within the continuous absorption band of oxygen. The points may be seen to lie along a straight line to within experimental error for total gas pressures ranging

[1] Herzberg, Zeits. f. physik. Chemie **4B**, 223 (1929).
[2] Schneider, Phys. Rev. **45**, 152 (1934).
[3] Kistiakowsky, J. Am. Chem. Soc. **52**, 1868 (1930).
[4] Warburg, Sitz. Akad. Wiss. Wien. 216 (1912); 872 (1914).

from 2.3 mm to 15.0 mm. Because of the high absorption at greater pressures, it was impossible to make accurate measurements beyond 15 mm of mercury. Since an increase in pressure increases the number of collisions between molecules, these experiments show that at low pressures an increase in the number of collisions has no effect on the absorption of oxygen in the Schumann region.

The slopes of the lines in Fig. 1 give the absorption coefficient for the nitrogen-oxygen mixture. When expressed in terms of the partial pressure of oxygen, the absorption coefficient for the maximum of the band, 1450A, is 0.55/cm/mm of mercury. Since the measurements were made at a temperature of 25° centigrade, the absorption coefficient reduced to normal temperature and pressure is 460 as compared with the value of 490 per cm at N.T.P. obtained by Ladenburg and Van Voorhis[5] for pure oxygen. The fact that these two values agree to within the experimental error shows that the addition of nitrogen had no influence on the absorption of the oxygen.

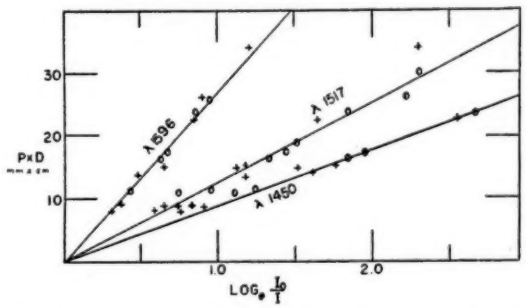

FIG. 1. The logarithm of the opacity of a mixture of 20 percent oxygen and 80 percent nitrogen as a function of the pressure in mm of mercury times the thickness. (0) represents a layer of gas 4.75 cm thick and (+) 2.27 cm.

[5] Ladenburg and Van Voorhis, Phys. Rev. **43**, 315 (1933).

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A Thermodynamic Treatment of Systems, in Particular of Solutions, from the Point of View of Activity and Related Functions

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The purpose of this paper is to present a consistent thermodynamic treatment of solutions based on activity and activity coefficient. On the basis of the argument presented interrelations of these quantities are obtained for dissociated and undissociated components. Expressions are also derived for the fugacity and activity of a component in a gas mixture.

IN 1878 Gibbs deduced an equation for dilute solutions. If this equation were to be redefined in terms of molar units, one of Gibbs' constants identified with the gas constant, and the resulting equation be assumed applicable over the whole range of concentration we would have the ordinary ideal solution definition. In application it was found in general that some solutions approximated very closely to this equation, others only when very dilute, and still others not at all. The latter type, namely solutions of electrolytes, were classified separately and a limiting law obtained by formally patching the existing one.

To extend the usefulness of this type of equation so that it might be applicable to all solutions and reduce to it when "infinitely" dilute and when "ideal," Lewis and Randall replaced the molar concentration factor by a function of the independent variables and named it activity, which was a truly inspired idea. The ratio of the activity to the molar concentration of the species, which they named activity coefficient, thus automatically cataloged all solutions in terms of deviations from the "ideal solution." This general pattern has, however, been partially concealed by their phraseology and some apparent ambiguity in defining their functions; as a result there have appeared in text books a variety of interpretations some of which are justifiable whereas others lead to mutually inconsistent interrelations of the ac-

tivities, in particular for dissociated and undissociated solutes.

In order to make the relations derived herein readily apparent the usual method of partially defining activity, a_i, of a component "i" in a binary system as a function of absolute temperature T, pressure p, and molar concentration X_i (such as mole fraction or molality), by the equation

$$a_i = e^{(F_i - F_i^0)/RT} = \phi_i e^{F_i/RT} \tag{1}$$

will be used. Here R denotes the gas constant, F_i (T, p, X_i) the molar chemical potential ($\mu_i M_i$ of Gibbs) for the state (T, p, X_i) and F_i^0 a quantity that makes the mole fraction activity equal to the mole fraction of "i" if the solution satisfy the equation of an "ideal" solution. The state for which $F_i = F_i^0$, i.e., $a_i = 1$, has been named the "standard state," and so F_i^0 could be called the molar chemical potential for the standard state. Considered from this point of view F_i^0 is, by definition, a function of both *temperature* and *pressure* and the "standard state" is free to vary in the (t, p) coordinate plane.

If the components of a solution were miscible in all proportions then a single expression would suffice to evaluate F_i^0 of each component but because complete miscibility is not in general obtainable in a solution F_i^0 (or ϕ_i) is evaluated separately for solvent and solute, denoted here by subscripts 1 and 2, respectively. The two equations are, however, limiting values of a single relation, namely the ordinary ideal solution definition.

In order to define ϕ_2 and thus F_2^0 of a solute the dilute solution law is assumed as a physical hypothesis, namely[1]

$$\frac{x_2}{1 - x_2} e^{-\mu_2/AT} = \phi(T, p), \tag{2}$$

where x_2 denotes the weight fraction of solute, μ_2 is Gibbs' chemical potential per gram. A, $(= R/M_2)$, is a constant for the particular solute (where M_2 denotes the mole weight of the species), and ϕ (T, p) is a function of T and p characteristic of the solute. The equation is to be considered as exact for the general case only when treated as a limiting law for $x_2 \to 0$. In terms of molar units Eq. (2), when treated as a limiting law, becomes

$$N_2 e^{-F_2/RT} = \phi_2(T, p), \tag{3}$$

where ϕ_2 (T, p) is a function of T and p characteristic of the substance. If Eq. (3) be extrapolated over the entire concentration range it becomes the usual definition of an ideal solution. If it be written in the logarithmic form its relation to the definition of activity will be evident. But Eq. (3) presupposes that a molecular weight has been chosen for the component to which it is ascribed, the molar concentration and molar chemical potential being expressed in terms of this mole weight. Therefore since F_2^0 of the solute activity will be defined in terms of this or a similar equation the solute activity so defined refers to the mole species chosen.

Empirically it is known that for undissociated solutes Eq. (3) expressed as a limiting law for $N_2 \to 0$ exists and here the corresponding mole fraction activity is defined such that

$$RT \ln \phi_2 = -F_2^0. \tag{4}$$

Other molar concentration units could also have been used, for example a common unit is molality, m, the number of solute moles in a kilogram of solvent. The molality activity is defined correspondingly such that

$$RT \ln \eta\phi_2 = -F_2^0, \tag{4a}$$

where η denotes the number of solvent moles per kilogram.

F_2^0 is therefore a function of T and p and, for different concentration units, will vary in absolute values.[2]

For strong electrolytes it is known that a limit does not exist if the formula weight of the undissociated solute be taken as the effective mole weight of the species. If the electrolyte is assumed, however, to be completely dissociated into its ion parts the mean effective mole weight of the average ion will be not the formula weight

[1] This is equivalent to Gibbs' Eq. (215). Cf. R. W. Goranson, *Thermodynamic Relations in Multicomponent systems*, Carnegie Inst. Washington Publ. No. 408 (1930), pp. 320–322.

[2] Falkenhagen (*Electrolytes*, translated by R. P. Bell, (Oxford, 1934), p. 55) equates the molality, mole fraction, and moles per liter of solution activities; his activities are therefore not equivalent to those of Lewis and Randall.

M_2 of the solute but M_2/ν if ν denotes the number of dissociated parts or ions.

Let a solute RS, if it dissociates, separate into ν parts or ions such that

$$RS \rightleftharpoons \sum_{i=1}^{\nu_+} R_i + \sum_{j=1}^{\nu_-} S_j. \tag{5}$$

One could then formally generalize the ordinary dilute solution equation and write the expression

$$N_i e^{-F_i/RT} = \frac{\phi_i'(T, p)}{k} = \phi_i(T, p) \tag{6}$$

for the ith species.

Herein $N_2 = (n_1/[n_1+n_2])$ denotes the mole fraction of solute where n_1 and n_2 are the number of moles of solvent and solute, respectively; N_2' denotes the mole fraction of undissociated solute and $N_\pm$ that of a mean species of dissociation, or

$$N_2' = \frac{(1-\alpha)N_2}{1+\alpha(\nu-1)N_2} \quad \text{and} \quad N_\pm = \frac{\alpha k N_2}{1+\alpha(\nu-1)N_2},$$

where α denotes the degree of dissociation and k is in general a constant for the particular solute. The participating or effective parts may be considered as (1) all distinct, $k=1$, (2) two distinct species, $k=[(\nu_+)^{\nu_+}(\nu_-)^{\nu_-}]^{1/\nu}$, or (3) one mean species, $k=\nu$. It is immaterial, however, which viewpoint be taken because Eq. (6) may be divided through by k and thus all three cases become equivalent in treatment so long as the relative proportions of the species remain constant. The relationships are simplified for molality concentrations, namely m, $m'=(1-\alpha)m$, and $m_\pm=\alpha k m$; here too the three cases will be made equivalent by dividing the corresponding equation through by k.

In many thermodynamic problems dissociated and undissociated states are not differentiated because to do so would serve no useful purpose. In such cases a quantity can be taken to denote the average molar chemical potential of a dissociated component RS, defined here by $\{F_2\}$, and which is equivalent to the sum of the molar chemical potentials of the parts which make up an average mole weight of solute in the solution. Thus if α denotes the degree of dissociation

$$\{F_2(T, p, N_2)\} = \sum_{i=1}^{\nu_+} F_i + \sum_{j=1}^{\nu_-} F_j = \nu F_\pm \text{ for } \alpha = 1, \tag{7a}$$

$$= (1-\alpha)F_2(T, p, N_2') + \alpha\nu F_\pm \quad \text{for } 0<\alpha<1, \tag{7b}$$

$$= F_2(T, p, N_2) \quad \text{for } \alpha = 0. \tag{7c}$$

The brace is used here to distinguish this quantity from the *chemical potential of the undissociated part* of the solute with which it might otherwise be confused.

Thermodynamically one cannot distinguish between the participating parts but obtains only the mean effect of the composite. Thus, when the variable is the concentration of the solute, a measure will be obtained of $\{F_2\}$ or of some value proportional to $\{F_2\}$ and not of any one constituent species; therefore, if there are ν parts and α remains unity, $\{F_2\}/\nu$ could be and is equivalent to the quantity generally assumed as the molar chemical potential of a mean ion or participating species.

If the condition given by Eq. (5) exists, such that $0<\alpha<1$, we have $F_2=\nu F_\pm$ and if this be combined with Eq. (7b) we have

$$\{F_2(T, p, N_2)\} = F_2(T, p, N_2') = \nu F_\pm(T, p, N_\pm). \tag{8}$$

It has just been demonstrated that the molar chemical potential $\{F_2\}$ of the solute in the solution is equivalent to the molar chemical potential F_2 of the undissociated part of the solute and this again equal to the sum of the molar chemical potentials of the species of dissociation or $\nu F_\pm$, assuming coexistence of these species. But unless the degree of dissociation and therefore the number of dissociated and undissociated moles of solute can be determined the concentrations N_2' and $N_\pm$ will not be known. Because ordinarily α is not known it is generally assumed that strong electrolytes are completely dissociated or that

$$N_2' = 0 \quad \text{and} \quad N_\pm = kN_2/[1+(\nu-1)N_2]. \tag{8a}$$

The ideal solution law will accordingly be written as

$$N_\pm e^{-\{F_2(T,\ p,\ N_2)\}/\nu RT} = \phi_\pm(T, p) \tag{9}$$

and for solutions sufficiently dilute so that N_2 and m can be considered as proportional to one another, in the form

$$m_\pm e^{-\{F_2\}/\nu RT}=\eta\phi_\pm(T, p)=\phi_\pm'(T, p), \quad (10)$$

where η denotes the number of solvent moles per kilogram.

If the assumption (8a) be made then changes in chemical potential which are the result of association will be included with other deviations from these solution "laws" and manifested as departures from "ideality."

It is known empirically that, for a solution of a strong electrolyte which is generally assumed to be completely dissociated, Eq. (9) or (10) exists only in the limit as N_2 or $m\to 0$. The mean ionic activity is then given by the expression $a_\pm(T, p, N_\pm)=\phi_\pm e^{\{F_2\}/\nu RT}$ and the activity of the undissociated solute by the expression $a_2(t, p, N_2')=\phi_2 e^{\{F_2\}/RT}$ so that

$$\frac{(a_\pm)^\nu}{a_2}=\frac{[\phi_\pm(T, p)]^\nu}{\phi_2(T, p)}=K(T, p) \quad \text{for } 0<\alpha<1, \quad (11)$$

and for an ideal solution defined as one satisfying Eqs. (3) and (9) then

$$\frac{(N_\pm)^\nu}{N_2'}=K(T, p), \quad (11a)$$

which is the equivalent of the law of mass action. If $\alpha=1$, as is ordinarily assumed for dilute solutions of strong electrolytes, then a_2 is, by definition, zero and Eqs. (5), (7) and therefore (11) do not exist. Thus $(a_\pm)^\nu$ is *not equal* to the activity a_2 of the *undissociated* solute as has sometimes been stated but may be correlated with a quantity defined as the average *activity of the solute* only if the latter be defined by the expression $\{a_2\}=(a_\pm)^\nu$.

The mole fraction and molality[3] "mean ionic" activity coefficients are defined by

$$\gamma_\pm(T, p, N_\pm)=\frac{[1+(\nu-1)N_2]a_\pm(T, p, N_\pm)}{N_2}$$

and

$$\gamma_\pm(T, p, m_\pm)=\frac{a_\pm(T, p, m_\pm)}{m},$$

respectively. If the solutions furthermore behave according to the ideal law as defined by Eq. (9)

$$\gamma_\pm(T, p, N_\pm)=\alpha\frac{1+(\nu-1)N_2}{1+\alpha(\nu-1)N_2} \quad \text{if } \alpha<1.$$

Thus for very dilute *ideal* solutions the value of $\gamma_\pm(T, p, N_\pm)$ may be regarded as equivalent to the degree of dissociation. The corresponding molality activity coefficient is given by

$$\gamma_\pm(T, p, m_\pm)=\frac{\alpha(1-N_2)}{1+\alpha(\nu-1)N_2} \quad \text{if } \alpha<1.$$

It is therefore a linearly decreasing function of the concentration N_2 and unity only in the limit as $m\to 0$.

The activity of the undissociated solute in solution, if *ideal*, would be given by

$$\gamma_2(T, p, N_2')=\frac{a_2(T, p, N_2')}{N_2}=\frac{1-\alpha}{1+\alpha(\nu-1)N_2}$$
$$=1-\gamma_\pm(T, p, N_\pm),$$

which is unity for $\alpha=0$ and zero for $\alpha=1$; and by

$$\gamma_2(T, p, m')=\frac{(1-\alpha)(1-N_2)}{[1+\alpha(\nu-1)N_2]}$$

which, for $\alpha=0$, is equal to $(1-N_2)$.

It is now a simple matter to evaluate the derivatives of F_2^0, the molar chemical potential of Lewis and Randall's "standard state" which has been defined by Eqs. (1) and (4), (4a), (9), or (10) as a function of T and p—a simple method is as follows. Differentiate Eq. (1) with respect to the independent variables T and p, then let the molar concentration m converge to zero as a limit and we obtain[4]

[3] This molality coefficient is equivalent to that of Lewis and Randall since here a is equivalent to their "a/k" where $k=[(\nu_+)^{\nu_+}(\nu_-)^{\nu_-}]^{1/\nu}$. (See reference 7.)

[4] Lewis and Randall do not write a pressure derivative of solute activity, in fact their only pressure derivative (reference 7, p. 255) relates to the activity of a simple substance. They do, however, say (reference 7, p. 259) of their standard solute state "the partial molal volume, heat content, and heat capacity are those of the solute at infinite dilution." Their intent seems therefore evident. Some writers (e.g., H. S. Taylor, Ed., *A Treatise on Physical Chemistry*, I (Harned, New York, 1931), p. 761), have assumed that Lewis and Randall's pressure derivative for a simple substance was also applicable for all activities, in which case F_2^0 would not be a function of pressure. Such an activity could readily be written by defining F_2^0 so that

$$\lim_{m\to 0}\frac{a_2(T, p, m)}{m}=\exp\int_1^p\frac{v_2^*}{RT}\,dp$$

$$\frac{\partial(F_2^0/RT)}{\partial T}=\lim_{m\to 0}\left[\frac{-H_2(T,p,m)}{RT^2}\right]$$

$$=-\frac{H_2^*(T,p)}{RT^2}, \quad (12a)$$

$$\frac{\partial(F_2^0/RT)}{\partial p}=\lim_{m\to 0}\left[\frac{v_2(T,p,m)}{RT}\right]=\frac{v_2^*(T,p)}{RT}, \quad (12b)$$

where H_2 denotes the partial molar heat content and v_2 the partial molar volume ($=\partial\mathbf{H}/\partial n_2$ and $\partial\mathbf{V}/\partial n_2$, respectively, where n_2 denotes the number of solute moles, $\mathbf{H}$ the total heat content (Gibbs' x) and $\mathbf{V}$ the total volume).

The activity and activity coefficient can now be written as the line integral[5]

$$\gamma_\pm(T,p,N_\pm)=\frac{a_\pm(T,p,N_\pm)}{N_\pm}$$

$$=\exp\int_{T_0,\ p_0,\ N_\pm=0}^{T,\ p,\ N_\pm}\frac{H_2^*-H_2}{\nu RT^2}dT+\frac{v_2-v_2^*}{\nu RT}dp$$

$$+\left[\frac{N_\pm}{\nu RT}\frac{\partial\{F_2\}}{\partial N_\pm}-1\right]d\ln N_\pm, \quad (13)$$

where $N_\pm=N_2/[1+(\nu-1)N_2]$ and $\exp A$ denotes e^A. This and the following line integrals represent the most general expressions and may be integrated over any path between the two limits. It can be broken up into three parts and because the limit of $\gamma_\pm$ as $N_2\to 0$ is, by definition, unity for all temperatures and pressures, it is possible to proceed from $(T_0,\ p_0,\ N_{\pm_0})$ to $(T,\ p,\ N_\pm)$ along constant T and p paths in which case the first two terms under the integral sign vanish; for example, in order to evaluate $\gamma_\pm(T,p,N_\pm)-\gamma_\pm(T_0,p_0,N_{\pm_0})$ one may integrate from $(T_0,\ p_0,\ N_{\pm_0})$ to $(T_0,\ p_0,\ N_\pm=0)$ and then from $(T,\ p,\ N_\pm=0)$ to $(T,\ p,\ N_\pm)$. If the temperature and pressure derivatives of $\gamma_\pm$ can be expressed as known functions of $(T,\ p,\ N_\pm)$ over the region considered then the difference $\gamma_\pm(T,p,N_\pm)-\gamma_\pm(T_0,p_0,N_{\pm_0})$ may be obtained by integrating Eq. (13) from $(T_0,\ p_0,\ N_{\pm_0})$ to $(T,\ p,\ N_\pm)$ without the necessity of evaluating either $\gamma_\pm(T_0,p_0,N_{\pm_0})$ or $\gamma_\pm(T,p,N_\pm)$.

The molality activity coefficient may be obtained by replacing $N_\pm$ by $m_\pm$ in Eq. (13) or by multiplying the right hand side of this equation by $(1-N_2)/[1+(\nu-1)N_2]$.

If the solute is not dissociated then ν is replaced by unity, $N_\pm$ by N_2, $a_\pm(T,p,N_\pm)$ by $a_2(T,p,N_2)$ and $\gamma_\pm(T,p,N_\pm)$ by $\gamma_2(T,p,N_2)$. The equation then conforms with Lewis and Randall's definition of the activity of an undissociated solute.

Solvent

The solvent activity is defined so that $F_1^0=F(T,p)$ where $F(T,p)$ denotes the molar free energy of the pure solvent substance.[6]

The mole fraction activity and activity coefficient can thus be evaluated as the line integral

$$\gamma_1(T,p,N_1)=\frac{a(T,p,N_1)}{N_1}$$

$$=\exp\int_{T_0,\ p_0,\ N_1=1}^{T,\ p,\ N_1}\frac{H-H_1}{RT^2}dT+\frac{v_1-v}{RT}dp$$

$$+\left[\frac{N_1}{RT}\frac{\partial F_1}{\partial N_1}-1\right]d\ln N_1. \quad (14)$$

This integral may be subdivided as was Eq. (13) and the same reasoning applied to it since, by definition, γ_1 has the same limit unity as $N_1\to 1$ for all values of T and p.

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if the "standard state" were assumed to be at the fixed pressure $p=1$. L. H. Adams (Chem. Rev. **19**, 1 (1936)) has interpreted their definition of activity as the latter alternative. (See reference 6.)

[5] If the differential form be preferred it can be obtained as follows: (a) for "$d\ln\gamma_\pm$" delete the "exp" and integral sign. (b) for "$d\ln a$" delete the "exp" and integral sign and cancel out "$d\ln N$" or "$d\ln m$," as the case may be, from each side of the equation. This method can be used for all the line integrals expressed in this paper but is not, however, applicable to line integrals in general.

[6] Lewis and Randall state "$a/N=1$ when $N=1$" and since a is in general a function of $(T,\ p,\ N_1)$ this would restrict F_1^0 to be a function of T and p only. However, they also state "if a pure liquid or a pure solid X at atmospheric pressure be chosen as the standard state of unit activity we may change the activity" by a change of concentration. This is presumably a slip but if not they should have said

$$\lim_{N_1\to 1}\frac{a_1(T,p,N_1)}{N_1}=\exp\int_1^p\frac{v}{RT}dp,$$

where v denotes the molar volume of the pure substance. It would be inconvenient for correlation purposes to have the solute and solvent defined unsymmetrically in this way and it is assumed here that the first quotation represents the intent of Lewis and Randall. This agrees with the pressure derivative as written by Schottky (W. Schottky, *Thermodynamik* (Berlin, 1929), p. 284). L. H. Adams has interpreted the definition of solvent activity as the second alternative which is symmetrical with his definition of solute activity.

If we wished to treat the solvent as a dissociated substance and consider the activity and activity coefficient of a mean resulting contributory part of the dissociated solvent, we could proceed as for a solute or by purely formal means substitute the symbol $\pm$ for the subscript "1" in Eq. (14) where $\pm$ denotes a mean solvent ion, and divide the right hand side of the equation through by ν with the exception of unity in the bracket.

We note then that, for systems miscible in all proportions, it is immaterial which of the two definitions we assign to the components because it is evident that the two definitions will express the same relation; here, however, the mole fraction will be the preferred unit of concentration because as N_2 approaches unity m becomes infinite.

Gas Mixtures

Gaseous constituents are miscible in all proportions and therefore a single expression will suffice to evaluate the activities of these components. An activity and activity coefficient of a gas component could then be defined by Eq. (13) or (14). It has been customary, however, to define for gases a quantity called fugacity.

An ideal binary gas mixture, by definition, satisfies the relations $p_i = N_i p$ and $F_i(T, p, N_i) = F(T, p_i)$, where p denotes the total pressure and p_i the pressure constituent i would have if it existed by itself at the same temperature and with the same value of its chemical potential. $F(T, p_i)$ denotes the free energy per mole of i at T and p_i. These relations, however, become applicable in general to real gas mixtures only for small values of p. The physical hypothesis will, accordingly, be written as

$$\lim_{p \to 0} pN_i e^{-F_i/RT} = \phi_i(T). \qquad (15)$$

The fugacity, f_i, of component i will be defined by Eq. (1), in which f_i replaces a_i, and the relation $RT \ln \phi_i(T) = -F_i^0$, and may be written as

$$\frac{f_i(T, p, N_i)}{pN_i} = \exp \int_{T_0,\ p=0,}^{T,\ p,\ N_i} \frac{H^* - H_i}{RT^2} dT + \left[\frac{pv_i}{RT} - 1\right] d \ln p + \left[\frac{N_i}{RT} \frac{\partial F_i}{\partial N_i} - 1\right] d \ln N_i, \qquad (16)$$

where H^0 is a function of T only.

When $N_i = 1$ then p denotes the pressure of the pure constituent i and the equation reduces to Lewis and Randall's[7] definition of fugacity for a simple gas; H_i and v_i become H and v, the heat content and volume per mole, respectively, and the last term vanishes.

If the activity, a_i, of a gas component i be defined by

$$a_i(T, p, N_i) = f_i(T, p, N_i)/f_i(T, p),$$

$f_i(T, p)$ denoting the fugacity of the pure constituent, it will be evident that this activity may be expressed by Eq. (14). When Eq. (3) is satisfied over the entire concentration range then $a_i/N_i \equiv 1$ and $f_i(T, p, N_i) \equiv N_i f_i(T, p)$. When Eq. (15) is satisfied over the entire pressure range then

$$f_i(T, p, N_i) \equiv N_i p.$$

In conclusion the writer wishes to acknowledge the helpful criticism received from L. H. Adams.

[7] G. N. Lewis and M. Randall, (*Thermodynamics and the Free Energy of Chemical Substances* (New York, 1923), p. 192), for their definition of F^0 "complete the definition by making the fugacity of a perfect gas equal to the pressure." For the argument it is not necessary to assume $|v - RT/p|$ converges to zero but merely that it remains finite as p converges to zero because we are concerned here with ratios, not differences.

The Deduction of Reaction Mechanisms from the Theory of Absolute Rates

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The limitations of the simple collision theory for reactions are discussed. The Menschutkin and related reactions are shown to involve the formation of an activated complex with an electric moment of a magnitude which is calculated for the various cases. The free energy of activation for proton transfer is found from the experiments on conductance in water and the dispersion effects on polarization in ice. A partition function for liquid H_2O and D_2O based upon experimental quantities is given. The abnormal rapidity of the denaturation of proteins in spite of an enormous activation energy is typical of reactions, involving the simultaneous breaking of many bonds.

INTRODUCTION

WE shall use as the general equation for the specific reaction rate constant[1]

$$k' = \frac{\kappa kT}{h}\frac{F_a'}{F_n}\exp(-E_0/kT) \qquad (1)$$

or the equivalent forms[2]

$$k' = \frac{\kappa kT}{h}K^{\ddagger} = \frac{\kappa kT}{h}K^{0\ddagger}\left(\frac{\alpha_1\alpha_2\cdots\alpha_n}{\alpha^{\ddagger}}\right)$$

$$= \frac{\kappa kT}{h}e^{-(\Delta H^{0\ddagger}/RT)}e^{\Delta S^{0\ddagger}/R}\left(\frac{\alpha_1\alpha_2\cdots\alpha_n}{\alpha^{\ddagger}}\right)$$

$$= \frac{\kappa kT}{h}e^{-(\Delta F^{0\ddagger}/RT)}\left(\frac{\alpha_1\alpha_2\cdots\alpha_n}{\alpha^{\ddagger}}\right)$$

$$= \frac{\kappa kT}{h}e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R} = \frac{\kappa kT}{h}e^{-(\Delta F^{\ddagger}/RT)}. \qquad (2)$$

The superscript zero indicates the standard state for the rate process. The other symbols are largely self-explanatory and in any case have been repeatedly defined in the literature so that we shall only define them here as use is made of them. If leakage through the barrier is important (but not too large) an additional factor $(1+1/24(h\nu_n/kT)^2)$ should be introduced into the above equations, where ν_n is the imaginary frequency associated with crossing the barrier.[3]

If leakage through the potential barrier is very great, as for example in the rapid oscillation of ammonia between the two mirror image forms, we can best start from the specific rate expression in the form proposed by Tolman,[4]

$$k' = \frac{\sum k_i\rho_i\exp(-E_i/kT)}{\sum\rho_i\exp(-E_i/kT)}, \qquad (3)$$

where k_i, ρ_i and E_i are specific rate, statistical weight and energy respectively for the ith level. This can be written in the more convenient form

$$k' = F_n^{-1}\left(\sum k_i\rho_i\exp\left(-\frac{E_i}{kT}\right) + \frac{\kappa kT}{h}F_a'\exp(-E_0/kT)\right), \qquad (4)$$

where we have added together the rates for the discrete levels and the continuum on our potential energy surface.

An interesting example of the solvent effect in preventing leakage is supplied by $^{-}CR_1R_2R_3$ which does not racemize in solution[5] but in the gas phase would probably racemize in a time not very different from the $\sim 10^{-10}$ seconds required for ammonia. Thus we know that this radical does not exist in the free state, and should not be thought of as uncombined with solvent or other

[1] H. Eyring, J. Chem. Phys. **3**, 107 (1935).
[2] *a*. Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935); *b*. Evans and Polanyi, Trans. Faraday Soc. **21**, 875 (1935).
[3] Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932).
[4] Tolman, *Statistical Mechanics*. (The Chemical Catalog Co., New York, 1927), p. 261. LaMer has used this equation to develop an expression for the temperature coefficient of the entropy of activation and related quantities; J. Chem. Phys. **1**, 289 (1933).
[5] Jones and Wallis, J. Am. Chem. Soc. **48**, 169 (1926).

molecules even for such very short times as 10^{-10} seconds.

The collision theory

It has been customary to interpret the specific reaction rate constant for bimolecular reactions by the equation

$$k' = PZ \exp(-E/RT) \tag{5}$$

where Z is the number of collisions calculated by using diameters more or less appropriate for momentum transfer, E is $RT^2 d \ln k'/dT$, and P is whatever is left over to make (5) true. Clearly there can be no objection to this on the basis of its correctness. The equilibrium constant for a reaction of the type

$$A + B = C + D \tag{6}$$

can be written as

$$K = \frac{k_i}{k_f} = \frac{P_i Z_i}{P_f Z_f} \exp((-E_i + E_f)/RT), \tag{7}$$

i.e.,

$$\frac{P_i Z_i}{P_f Z_f} = \exp(\Delta S/R). \tag{8}$$

Here the subscript f refers to the final products and i to the initial reactants. The E's are defined as in (5). Since, in any actual case,

$$\Delta S = \int_0^T \Delta C_p dT/T$$

always depends on the temperature while Z_i/Z_f does not, then P_i/P_f must. Equating K of (7) to the statistical expression, one obtains

$$K = (F_f/F_i) \exp(-E_0/RT), \tag{9}$$

where F_i and F_f are the partition functions for the initial and final states and E_0 is the excess energy of the final over the initial states at the absolute zero of temperature. The point to be emphasized is that (9) shows that K is inversely proportional to all the properties of the initial molecules, such as their diameters, frequencies, etc., which enter into the partition function F_i, while in (8), since the momentum transfer diameters are used, K is calculated as directly proportional to the collision diameters of the initial molecules. The two equations are to this extent contradictory and of course (9) is correct. If one tries to remedy this by taking the reaction rate proportional to the actual diameters in the activated state and inversely proportional to those in the normal state, as one must as indicated in (9), one can get Eq. (1), but there then isn't much left of the collision theory in its original form.

In spite of these logical difficulties the collision theory is useful if it provides a way of estimating reaction rates with reasonable accuracy. It certainly will not give the rate correctly in both directions, however, unless it leads to the right value for the equilibrium constant. This is by no means a sufficient condition for a reaction theory to satisfy, but it is a necessary one. As an example we calculate the equilibrium constant for the reaction $H_2 + I_2 = 2HI$ by both methods. Statistical mechanics gives

$$K = \frac{4r_3^4}{r_1^2 r_2^2} \frac{m_3}{(m_1 m_2)^{\frac{1}{2}}} \exp\left(\frac{2S_3 - S_1 - S_2}{R}\right) \times \exp\left(-\frac{\Delta H}{RT}\right), \tag{10}$$

where the entropy of vibration

$$S_i = R\left[\frac{h\nu_i/kT}{\exp(h\nu_i/kT) - 1} - \ln\left(1 - \exp\frac{-h\nu_i}{kT}\right)\right].$$

The collision theory gives

$$K = \frac{2\sigma_{1,2}^2}{\sigma_3^2} \frac{m_3}{(m_1 m_2)^{\frac{1}{2}}} \exp(-\Delta H/RT). \tag{11}$$

Here the subscripts 1, 2 and 3 refer to H_2, I_2 and HI, respectively, and r, σ, m, ν, and ΔH are the distance between atoms in the molecule, the collision diameter, molecular mass, molecular frequency and change in heat content, respectively. At 0°A Eq. (10) yields $K = 37.4 \exp(-\Delta H/RT)$, while, taking $\sigma_{1,2}^2 = \sigma_3^2$ (which seems as good a guess as any) we get from equation (11) $K = 11.35 \exp(-\Delta H/RT)$. At 440°C the collision value has not changed, while the correct expression has been decreased by the term $\exp(-S_2/R)$ to $K = 5.88 \exp(-\Delta H/RT)$. This is not bad agreement with the collision theory value, and would be better at a higher temperature and of course much worse at lower ones. At constant volume $\Delta E = \Delta H$.

Since the activated complex is the same for the forward and the reverse reactions, it is possible to choose $\sigma_{1,2}^2=\sigma_3^2$ equal to some value r^2 such that one gets correct rates in one direction and almost the correct ones in the other, i.e., within a factor of 3 at 440°C. At least for some reactions r is about the kinetic theory collision diameter at reaction temperatures. For other reactions such a value of r^2 will not be even approximately correct. The equilibrium $N_2+O_2=2NO$ illustrates one other shortcoming of the simple collision theory.[5a] In this case the entropy corresponding to the additional factor $(2+4\exp(-343.8/RT))^2$ must be introduced into (10) for the electronic states in the NO molecules. Thus, at 27°C statistical mechanics gives the value $K=297\exp(-\Delta H/RT)$, while the collision theory gives $K=2\exp(-\Delta H/RT)$. Certainly there is a better way of estimating (PZ) than the collision theory for Z and no theory for P. Even if we had to guess the properties of the activated complex, just as we must guess collision diameters in the kinetic theory, at least by using (1) we avoid the inconsistencies of the collision theory. Eq. (1) necessarily leads to correct equilibrium constants for reactions. For further examples of large P's in gas reactions see a paper by Bawn.[6]

In view of these considerations it must be clear that the procedure of taking a standard Z factor for gas reactions is of very doubtful significance. In the liquid phase there are added complications. It has been recognized that for reactions where the reactants are ionized while the products are not the same Z for both reactions is not to be expected. However, it has often been assumed that where two reactions are of the same type with respect to charge the Z's and the P's should be at least nearly the same, i.e., for such an equilibrium there should be very little change in entropy (cf. Eq. (8)). This is occasionally, but by no means always, true as Table I for proton migration reactions shows. The data in Table I were calculated from the work of White and Jones.[7] Many more are available but the above suffice for our purpose.

The first ten of these reactions simply involve the transfer of a proton from some negative ion to one of its isomers, and should therefore fulfill the criteria for "similar reactions" as well as possible. $\Delta S=4.6$ e.u. corresponds to a ratio of 10 for the factor P_iZ_i/P_fZ_f. The assumption that this factor should be unity (nearly) for similar reactions is satisfactorily fulfilled in the case of reaction 9, but fails by factors of from 3 to 30 for the other ten reactions. In each of the first six reactions there is the alternative of hydrogen bonds forming between a carboxylate ion and some other group such as NH_2, COOH, OH, inside the molecule or forming this bond with the surrounding water molecules. The first alternative, if a satisfactory bond can be formed, will lead to the higher entropy for the dissolved acid molecule. This explains the higher entropies of the *ortho* over the corresponding *meta* ions, and that of the *meta* over the *para*, and of the *cis* over the *trans*. In the toluic acids where no internal hydrogen bond is possible the situation is reversed. Reaction (11) is about as serious a violation of the simple collision theory as we have found in this type of reaction. Here $P_iZ_i/P_fZ_f=2.5\times10^{-6}$. Thus if this reaction obeys the collision theory in one direction it is off by almost a million times in the other. If the same collision diameter be taken for reactants as for products then the calculated value of Z_i/Z_f will be practically unity. It is not possible here to throw the responsibility for the small P on some nonthermodynamic quantity (such, for example, as failure to dissipate the activation energy). The different rates arise, rather from the fact that when butyric acid ionizes, the surrounding solvent molecules have the forces holding them increased by much more than do the water

TABLE I. *For reactions of the type:* $acid_1+ion_2=ion_1+acid_2$.

No.	Acid	Ion	ΔS	ΔH	K
1	*o*-amino-benzoic	*p*-amino-benzoate	6.29	1912	0.94
2	metanilic	sulfanilate	0.87	969	0.304
3	maleic	fumarate	4.84	−179	15.25
4	citraconic	mesaconate	3.23	42	4.70
5	salicylic	*m*-hydroxy-benzoate	5.87	208	13.28
6	salicylic	*p*-hydroxy-benzoate	6.79	−128	37.19
7	*o*-toluic	*m*-toluate	−3.19	−1484	2.45
8	*o*-toluic	*p*-toluate	−3.89	−1849	3.16
9	*n*-butyric	isobutyrate	0.16	26	1.034
10	*p*-toluic	phenylacetate	2.28	818	0.794
11	*n*-butyric	metanilate	−24.51	−5777	0.077
12	sulfanilic	hydroxide	17.62	−9775	6.55×10^{10}
13	acetic	hydroxide	−3.57	−13750	1.8×10^{9}

[5a] Gershinowitz and Eyring, J. Am. Chem. Soc. **57**, 985 (1935).
[6] Bawn, Trans. Faraday Soc. **32**, 178 (1936).
[7] White and Jones, Am. Chem. J. **44**, 159 (1910).

molecules surrounding the metanilic acid when its ionization occurs. Thus an ice-like sheath gathers round the butyrate ion as it forms. This sheath is at a lower "effective" temperature and is thicker than that which forms when metanilic acid ionizes. This is because in the latter ion the charge can distribute itself over a larger volume through a reorganization of the bonds in the aromatic residue, i.e., resonance between the different bond structures. The larger the sphere over which a charge is distributed the less the force with which surrounding molecules are held and the less the decrease in entropy as the ion is formed. We can then state the general proposition. *Any ion which can resonate between a variety of bond structures is provided with a mechanism which distributes the charge over a larger volume thus reducing the potential at the surface of the ion and therefore the binding with the solvent. As a result such ions exhibit a comparatively low entropy of ionization.* Conversely the entropy of ionization provides a criterion of the amount of internal bonding of a type not seriously restricting the freedom of relative motion of the parts which form the ion. This last qualification is necessary, since, for example, a hydrogen bond between two points on a long chain decreases the entropy more than if the two points made bonds with the solvent.

Frequently a reaction shows marked changes in the "collision factor" with a change in solvent. In general this is accompanied by a compensating change in the activation energy with the result that the over all change in rate is comparatively small. Using the language of Eq. (2) we can say that an increase (or decrease) in the entropy of activation, $\Delta S^{\ddagger}$, is in general accompanied by a more or less completely compensating change in the heat of activation, $\Delta H^{\ddagger}$, which leaves the free energy of activation, $\Delta F^{\ddagger}=\Delta H^{\ddagger}-T\Delta S^{\ddagger}$, but slightly changed. The explanation of this may be seen as follows: Suppose first we have the case in which two ions with unlike charge (or two polar molecules) combine to form a neutral molecule (or one with a smaller dipole moment). In polar solvents the ions will, of course, tend to be more solvated than the activated complex. This will result in a large value for the absolute entropy of activation. The point to be explained is why the changing of solvation by changing to a new solvent will affect $\Delta F^{\ddagger}$ much less than it affects $\Delta S^{\ddagger}$. When a liquid solidifies by freezing there is a large decrease in both the entropy and the heat content without *any* change in the free energy, the one exactly compensating the other. Now if all the forces between the molecules could be increased, the liquid would freeze at some higher temperature with, however, this same compensation between heat content and entropy. This is just what an ion or dipole does when it is introduced into a polar solvent. It increases the forces acting on neighboring solvent molecules, and if this increase is great enough, and the temperature not too far above the melting point of pure solvent, a certain number of solvent molecules "freeze," thus decreasing the entropy of the system but giving off a compensating heat of solidification which more or less completely balances the entropy change. Thus in transferring a mole of ions from one solvent to another where the forces between ions and solvent molecules will in general be different and where solvent melting points are different, there will, on the whole, be a different amount of solvent frozen before and after the transfer. This results in comparatively large changes in the partial molal heat content and entropy and a comparatively small change in the partial molal free energy. Thus, if $\mathbf{S}_{ij}$ is the partial molal entropy associated with taking a mole of reactant i from the gas phase and introducing it into solvent j, and if $\mathbf{S}_j^*$ is the same quantity for the activated complex, then the entropy of activation, $\Delta S^{\ddagger}$, in solvent j exceeds that in solvent k by the quantity

$$\Delta S_j^{\ddagger}-\Delta S_k^{\ddagger}=\mathbf{S}_j^*-\sum_i\mathbf{S}_{ij}-(\mathbf{S}_k^*-\sum_i\mathbf{S}_{ik})$$
$$=\mathbf{S}_j^*-\mathbf{S}_k^*-\sum_i(\mathbf{S}_{ij}-\mathbf{S}_{ik}). \quad (12)$$

Further

$$P_jZ_j/P_kZ_k=\frac{\kappa_j}{\kappa_k}\exp\left(R^{-1}(\Delta S_j^{\ddagger}-\Delta S_k^{\ddagger})\right). \quad (13)$$

Here κ_j and κ_k are the transmission coefficients in solvents j and k, respectively. If a reaction involves changes in multiplicity, the paramagnetism of the two solvents would have an important effect on the κ values. Conceivably, also, the κ values may vary considerably due to a difference in the facility with which solvent molecules supply or absorb the energy of activa-

tion, but in the great majority of reactions in solution the important factor influencing this ratio seems to be exp $(R^{-1}(\Delta S_j^{\ddagger}-\Delta S_k^{\ddagger}))$. Understanding this factor, as we have seen, reduces simply to understanding the change in partial molal entropy with change in solvent for the activated complex and for the reactants. Equations exactly analogous to (12) can be written for the difference in heat content and free energy in two solvents.

$$\Delta H_j^{\ddagger}-\Delta H_k^{\ddagger}=\mathbf{H}_j^{*}-\mathbf{H}_k-\sum_i(\mathbf{H}_{ij}-\mathbf{H}_{ik}), \quad (14)$$

$$\Delta F_j^{\ddagger}-\Delta F_k^{\ddagger}=\mathbf{F}_j^{*}-\mathbf{F}_k^{*}-\sum_i(\mathbf{F}_{ij}-\mathbf{F}_{ik}). \quad (15)$$

For the relative specific rates in the two solvents we obtain

$$k_j'/k_k'=(\kappa_j/\kappa_k)\exp((RT)^{-1}(-\Delta F_j^{\ddagger}+\Delta F_k^{\ddagger})). \quad (16)$$

It is of interest to examine the experimental work of Muchin, Ginsberg and Moissejewa[8] who measured the rate of the addition reactions pyridine to benzyl bromide and triethyl amine to benzyl bromide to give the two corresponding salts. These reactions were each measured in benzene-alcohol mixtures and also in benzene-nitrobenzene mixtures, where the mole fractions of the solvent components were varied from 1 to 0. The free energy of activation

$$\Delta F^{\ddagger}=-[RT\ln k'-RT\ln kT/h] \quad (17)$$

of these are plotted against the reciprocal of the dielectric constant, $1/D$, in Fig. 1. Curve III of Fig. 1 is based on the work of de Hemptinne and Bekaert[9] on the Menschutkin reaction $((C_2H_5)_3N+C_2H_5Br\rightarrow)$ measured in a benzene-acetone solvent, the mole fraction of both components being varied from 1 to 0. All the values are for 27°C, and the transmission coefficient, κ, is taken as unity. The free energies of activation are plotted against $1/D$ since the Debye Hückel theory gives the expression

$$\frac{Ne^2}{2Da}-\frac{Ne^2}{3D}\left(\frac{4\pi\epsilon^2}{DkT}\sum_i n_i z_i^2\right)^{\frac{1}{2}} \quad (18)$$

for the electrical work required to charge a mole of ions N. Here a, e, ϵ, n_i, z_i are the radius of the ion, its charge in electrostatic units, the charge on an electron, the number of ions of type i per cc, and the charge on the ith ion in multiples of the unit charge. At the beginning, at least, of the above reactions the last term of (18) is negligible, there being no ions. If we extrapolate curve IV (Fig. 1) to $1/D=0$ we get 22.07 kcal. for the free energy of activation, while at $1/D=1$ we get 25.65 kcal., an increase in $\Delta F^{\ddagger}$ of 3.58 kcal. for the electrical part of the free energy of activation if it were carried out at unit dielectric constant, i.e., in the gas phase, as compared with its value if carried out in a solvent of infinite dielectric constant. We compare this value with $Ne^2/a=329.5/a$ kcal., the energy of charging up two ions with radii of a angstroms in a medium of unit dielectric constant. Since, if ions were formed, the ionic radii would not exceed a few angstroms and so give a very large energy of charging, the process of activation clearly does not involve the formation of ions, but does involve a considerable increase in the electric moment of the reactants. We next modify Kirkwood's Eq. (26) slightly[10] to obtain the electrical part of the free energy for a multipole, and combine such expressions for the reactants and the activated complex to obtain the free energy of activation, $\Delta F_D^{\ddagger}$ in a solution of dielectric constant D, where the value $\Delta F_1^{\ddagger}$ is the value in a solution of dielectric constant 1. The relation is

$$\Delta F_D^{\ddagger}=-N/2\sum_{n=0}^{\infty}\frac{(n+1)(D-1)}{(n+1)D+n}\times\left[\frac{Q_n^{*}}{b^{*2n+1}}-\sum_i\frac{Q_{ni}}{b^{2n+1}}\right]+G+\Delta F_1^{\ddagger}, \quad (19)$$

where the term G is the part of the free energy change (in going from $D=1$ to $D=D$) not depending on the electrostatic forces. Thus the relative solubilities of the reactants and the activated complex will change with composition of solvent due to changes in the van der Waals' forces and chemical combination with the solvent, and so contribute to G. Such effects are discussed in detail by Hildebrand.[11]

[8] Muchin, Ginsberg and Moissejewa, Chem. Zentr. II, 2376 (1926).

[9] de Hemptinne and Bekaert, Zeits. f. physik. Chemie **28**, 225 (1899).

[10] Kirkwood, J. Chem. Phys. **2**, 351 (1934). See also R. E. Bell, Trans. Faraday Soc. **27**, 797 (1931).

[11] Hildebrand, *Solubility* (Reinhold Publishing Co., New York, 1936).

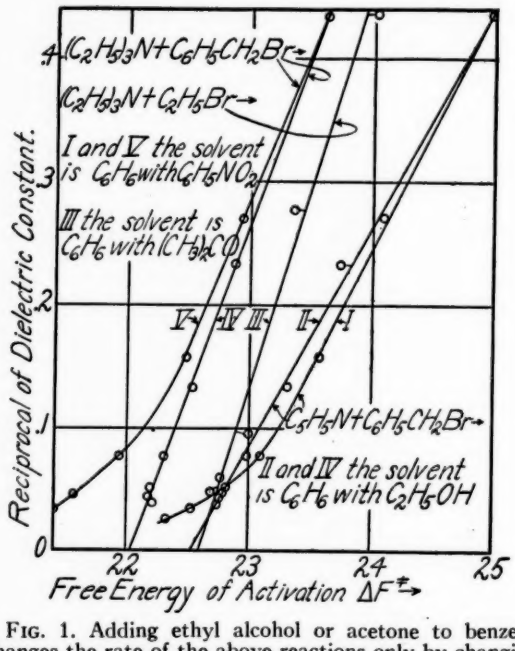

FIG. 1. Adding ethyl alcohol or acetone to benzene changes the rate of the above reactions only by changing the dielectric constant. Nitrobenzene has an additional effect.

In (19) N, D, b_i and b^* are Avogadro's number, dielectric constant, the radius of the hypothetical sphere from which a reactant molecule excludes solvent molecules, and the same radius for the activated complex. The subscript i is to be summed over all the reactants and the asterisk indicates the activated complex.

For a molecule with two charges, $+e$ and $-e$, separated by a distance R and situated at equal distances, r, from the center of a spherical molecule with radius b, Kirkwood finds:

$$Q_0=(\sum e_i)^2=0,$$
$$Q_1=\mu^2=\epsilon^2R^2,$$
$$Q_2=3\mu^2(r^2-R^2/4),$$
$$Q_3=6\mu^2(r^4-5r^2R^2/8+5R^4/48).$$

μ and ϵ are the electric moment of the molecule and the charge on the electron, respectively.

$$\text{Now}\quad \frac{\partial(\Delta F_D^{\ddagger})}{\partial(1/D)}=\frac{ND^2}{2}\sum_{n=0}^{\infty}\frac{(2n+1)(n+1)}{((n+1)D+n)^2}\times\left[\frac{Q_n^*}{b^{*2n+1}}-\sum_i\frac{Q_{ni}}{b_i^{2n+1}}\right]+\frac{\partial G}{\partial(1/D)}. \quad (20)$$

From (20) we see that when $\partial G/\partial(1/D)$ can be neglected and when D is reasonably large compared with the highest n that need be considered, then $\Delta F_D^{\ddagger}$ is a linear function of $1/D$. The reaction of benzyl bromide with triethyl amine and with pyridine in solvents varying from pure benzene to pure alcohol satisfy this linear relationship quite well. The same reactions are approximately linear up to moderate concentrations of nitrobenzene in benzene. We shall therefore use the following modification of (20) to estimate μ^* of the activated complex from the slope of $\Delta F^{\ddagger}$ against $1/D$ at the point $D=5$. All Q's except Q_1 have been neglected since, in the reactions under consideration this is probably a good approximation.

$$\frac{\partial(\Delta F_D^{\ddagger})}{\partial(1/D)}=\frac{24N^2D^2}{(2D+1)^2}\left[\frac{\mu^{*2}}{V^*}-\frac{\mu_1^2}{V_1}-\frac{\mu_2^2}{V_2}\right]. \quad (21)$$

Here b, the hypothetical molecular radius, has been estimated by means of the equation $8b^3N=V$. Using (21) we calculate the values for μ^* given in Table II. Here the subscript 1 refers to pyridine in I and II, and to triethyl amine in the other three. The subscript 2 indicates ethyl bromide in III and benzyl bromide in the remaining reactions. V^* is taken as the sum of the molal volumes of the reactants. Without a knowledge of the effect of pressure on reaction rate, or a calculation of the potential surface, this is the best we can do as an estimate of V^* and is probably not far from right. The fifth column gives the amount by which the free energy of activation in the gas phase would exceed that in a solvent of infinite dielectric constant if $\partial F^{\ddagger}/\partial(1/D)$ were constant and had the value possessed at $D=5$. If the dielectric constant of the solvent and the moments of the reactants and activated complex were the whole story, then simply changing the solvent should make no difference in the values in column 5, i.e., I is to be compared with II and IV with V. At least, at $D=5$ the change in dielectric constant seems to be the principal effect. At high concentrations of nitrobenzene (see Fig. 1) some additional factor enters which seems best interpreted as compound formation between the activated complex and the nitrobenzene. This might have been anticipated since the plot of dielectric constant against mole fraction of nitrobenzene when mixed with benzene shows a rise considerably more rapid than linear, indi-

cating association of the nitrobenzene. Such association may well be considerably more pronounced with a very polar substance such as the activated complex. Compound formation should be signalized by $\Delta S^{\ddagger}$ becoming rapidly more negative with the added nitrobenzene and $\Delta H^{\ddagger}$ decreasing and over compensating the entropy change. Fig. 2 shows that this is what happens in the case of pyridine reacting with benzyl bromide in a benzene-nitrobenzene solvent. Similar effects are present in the other cases. The significance of this for the "collision number" has already been discussed.

The values found for μ^* as given in the last column of Table II are near those to be expected for the resultant molecule. Thus the activated complex must have very nearly the same configuration as the final molecule. That this is true in a closely similar reaction can be shown by comparing the entropy of activation and the entropy of reaction. Thus Essex and Gelormini's results[12] for the reaction

$$C_6H_5N(CH_3)_2+CH_3I=C_6H_5N(CH_3)_3I$$

give $\Delta S^{\ddagger}=-36.1$ and $\Delta S=-37.06$ at 60°C.[13]

This also indicates that the activated configuration is very like the final one.

If ions are added to the reacting system we must add another term to (19) depending on the ionic strength. We then obtain

$$F_D^{\ddagger}=-\frac{N}{2}\sum_{n=0}^{\infty}\frac{(n+1)(D-1)}{(n+1)D+n}\left[\frac{Q_n^*}{b^{*2n+1}}-\sum_i\frac{Q_{ni}}{b^{2n+1}}\right]+\Delta F_1^{\ddagger}+G+RT\ln\frac{\gamma^*}{\prod_i\gamma_i}, \quad (22)$$

where we refer back to Kirkwood's Eq. (21) for the explicit form of γ.

Reactions Involving the Breaking of Hydrogen Bonds[14]

Bernal and Fowler[15] have given arguments for thinking of ice as possessing a structure such that each oxygen is surrounded by four hydrogen atoms at approximately tetrahedral angles. Two of these hydrogen atoms are to be thought of as belonging to a particular oxygen atom and are about 0.95A from it—the normal distance in steam—and the other two are about 0.86A further away and belong to neighboring oxygens.[16] This same structure is assumed to persist in water near the melting point and to be superseded by a state of increasing disorder with rising temperature. Ionization results when an oxygen gains a third near hydrogen by one of its two far neighbors coming 0.86A closer, leaving an O^-H behind. The H_3^+O can now lose an H^+ to each of three neighbors. The return migration of the one proton simply reverses the ionization. However, migration of the other two corresponds to migration of the H_3^+O and by repetition of the process the positive charge can travel to a distant electrode. In a similar way O^-H by acquiring neighboring protons can transfer the negative charge to any distance. This process of a negative ion acquiring a proton from a neutral molecule is the type reaction considered in Table I, so that the free energy of activation $\Delta F^{\ddagger}$ is a matter of considerable interest. The migration of a proton from H_3^+O to a neutral molecule is also of very wide occurrence. It is therefore important to ascertain what value the conductance gives for the free energy of activation.

If direct current is to be carried through water by proton transfer then since protons are liberated at one electrode and oxygen at the other, the process will come to a standstill unless some mechanism exists whereby protons after having passed from one oxygen to a neighboring one are then able to pass this oxygen. The rotation of molecules provides such a mechanism. Thus a combination of proton transfer with rotation of

Table II.

Reaction	V_1	V_2	V^*	$\frac{\partial(\Delta F^{\ddagger})}{\partial(1/D)}$ cal.	$\mu_1\times10^{18}$	$\mu_2\times10^{18}$	$\mu^*\times10^{18}$
II	80.5	118.9	200	5650	2.1	1.81	6.52
I	80.5	118.9	200	5050	2.1	1.81	6.30
IV	139.9	118.9	259	3650	0.8	1.81	5.48
V	139.9	118.9	259	4075	0.8	1.81	5.71
III	139.9	76.2	216	3150	0.8	1.83	5.11

[12] Essex and Gelormini, J. Am. Chem. Soc. **48**, 882 (1926).

[13] Wynne-Jones and Eyring (J. Chem. Phys. **3**, 492 (1935)) give too large a value for ΔS because of an incorrect interpretation of the equilibrium results of Essex and Gelormini.

[14] W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. **42**, 1419 (1920).

[15] Bernal and Fowler, J. Chem. Phys. **1**, 515 (1933).

[16] Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).

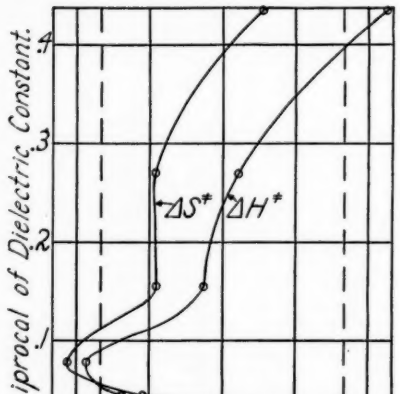

FIG. 2. Changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ nearly compensate each other.

molecules constitutes one mechanism of conductance in water while the usual bodily transport of the ion is another.

Huckel,[17] Bernal and Fowler[15] and Wannier[17a] have discussed this process. If the barrier which the proton passes over is flat a classical treatment is sufficient for the reaction rate. If it were high, since it is certainly thin, quantum-mechanical leakage would be important and as Bernal and Fowler point out the abnormally large mobility of the hydrogen ion would in that case not be present for deuterium ion. Subsequently, Lewis and Doody[18] have shown that K^+, Cl^- and acid ion have the mobilities 64.2, 65.2 and 315.2, respectively, in ordinary water and 54.5, 55.3 and 213.7 in heavy water. Thus the $D_3{}^+O$ ion has nearly as great a mobility relative to K^+ and Cl^- as $H_3{}^+O$ has so that we are dealing with a very flat barrier. We therefore calculate the height of the potential barrier neglecting quantum mechanical leakage by a method similar to that of Huckel. Our treatment differs slightly from his in that we regard rotation of the molecules and proton transfer as two successive steps of the same process. The slower of the two steps is the rate determining one.

We first consider the frequency k' at which a proton crosses a barrier under an effective potential gradient of B. Using the theory of absolute reaction rates we obtain:

$$k'=(\kappa kT/h)\exp\left(-(\Delta F^{\ddagger}-B23{,}060\cos\theta\, 0.43\times10^{-8})/RT\right).$$

Here 0.43×10^{-8} is the distance to the top of the energy barrier, i.e., half the distance the proton must travel in crossing a symmetrical barrier. θ is the angle which the particular hydrogen bond in question makes with the potential gradient. The factor 23,060 converts electron volts to calories. Effectively the distance the charge travels after the $H_3{}^+O$ has rotated is from one oxygen center to the next, i.e. $[18(6.06\times10^{23})^{-1}]^{\frac{1}{3}}=3.1\times10^{-8}$A. This distance must be multiplied by $\cos\theta$ to give the distance traveled along the potential gradient. The average distance per second along the gradient which the charge is carried by each proton on $H_3{}^+O$ is (averaging over all angles θ) then

$$(\kappa kT/h)\exp(-\Delta F^{\ddagger}/RT)\int_0^{\pi}\exp(B23{,}060\cos\theta\times0.43\times10^{-8}/RT)\cos\theta\sin\theta d\theta\times\left(\int_0^{\pi}\sin\theta d\theta\right)^{-1}=(\kappa kT/h)\times\exp(-\Delta F^{\ddagger}/RT)3.1\times10^{-8}\,23{,}060B\times0.43\times10^{-8}(RT)^{-1\frac{1}{3}}.$$

The three protons give three times this value for $H_3{}^+O$. The molal conductance due to proton transfer is then

$$\Lambda'=96{,}500(\kappa kT/h)\exp(-\Delta F^{\ddagger}/RT)\times\frac{3.1\times0.43\times23{,}060\times10^{-16}B}{RT}=3.106\times10^{3}\,\kappa B\exp(-\Delta F^{\ddagger}/RT).\quad(23)$$

We take the transmission coefficient $\kappa=1$. By using (23) with Huckel's estimate for $(\Lambda_H-\Lambda_{Na})$ as the molal conductance due to proton transfer Λ' where Λ_H and Λ_{Na} are the measured molal conductance of $H_3{}^+O$ and Na^+, respectively, we obtain Table III.

There is considerable uncertainty as to what value should be taken for B the effective potential gradient along the potential barrier when the overall potential gradient is one volt per centi-

[17] E. Huckel, Zeits. f. Electrochemie **34**, 546 (1928).
[17a] C. Wannier, Ann. d. Physik **24**, 545 and 569 (1935).
[18] Lewis and Doody, J. Am. Chem. Soc. **55**, 2616 (1933).

meter.[19] Huckel assumed $B=(D+2)/3$ where D is the dielectric constant which varies from 88.2 at 273°K to 47.1 at 429°K. Using this relationship at 298°K where $D=78.8$ we obtain $\Delta F^{\ddagger}=3350$ cal. Now if the slow process is the rotation of the molecules our formal expression for Λ' would be but slightly changed and consequently we would obtain nearly the same value for $\Delta F^{\ddagger}$. Since we are measuring the slow process it seems clear that the free energy of activation for the reaction $H_3{}^+O+H_2O=H_2O+H_3{}^+O$ is less than 3.5 kcal. and lies between this value and 1 kcal. The same treatment of the conductance of O^-H will give a $\Delta F^{\ddagger}$ for the reaction $H_2O+O^-H\rightarrow O^-H+H_2O$ lying in this same range. The next to last row in Table III gives the heat of activation calculated from successive pairs of points if B could be taken equal to unity. Otherwise it must be corrected for the temperature dependence of B.

We next consider the relaxation time in ice as revealed by the dispersion of the dielectric constant.[20] Murphy[21] found that if τ expresses the relaxation time of the polarized condition of the dielectric that the dispersion formulae obeyed in ice are

$$\epsilon'=\epsilon_\infty+\frac{\epsilon_s-\epsilon_\infty}{1+\omega^2\tau^2} \quad \text{and} \quad \epsilon''=\frac{(\epsilon_s-\epsilon_\infty)\omega\tau}{1+\omega^2\tau^2},$$

where ϵ' and ϵ'' are the real and the imaginary parts of the dielectric constant respectively. These are the formulae Debye showed[22] apply to rotation of molecules if the relaxation time of the individual molecules is given by

$$\tau_1=\frac{\epsilon_\infty+2}{\epsilon_s+2}\tau. \tag{24}$$

Here ω is 2π times the frequency of the applied potential ϵ_s and ϵ_∞ are the dielectric constants for static and infinite frequency respectively. Murphy points out that the same formulae apply to a variety of types of polarization.

We shall now consider what Debye's model of dipoles orienting in an electric field enables us to say about the relaxation time. We write

$$\tau_1{}^{-1}=k'=\frac{\kappa kT}{h}e^{-(\Delta F^{\ddagger}/RT)} \tag{25}$$

the specific reaction rate for rotation. From (25) and Murphy's value of τ calculated from $\partial(\epsilon''/(\epsilon'-\epsilon_\infty))/\partial\omega$ we obtain Table IV.

In calculating τ_1 we used $\epsilon_\infty=2.2$ and used Murphy's Table II, column 5, to get ϵ_s. There is the same kind of uncertainty in the formula to be used for calculating τ_1 from τ that existed in the B for conductance. We, however, use the formula (24) proposed by Debye. Larger values of τ_1 of course would mean larger $\Delta F^{\ddagger}$ values. The values calculated from Smyth and Hitchcock's experiments agree quite closely with Murphy's in spite of a considerable difference in the purity of the water used and in methods of measurement.

The free energy of ionization of water at the freezing point is $\Delta F=18.68$ kcal. Hence

$$\frac{(H_3{}^+O)(O^-H)}{(H_2O)^2}=e^{-(\Delta F/RT)}$$

and if $(H_3{}^+O)=(O^-H)$ then $(H_3{}^+O)/(H_2O)=e^{-(\Delta F/2RT)}$. Now the concentration of ions in ice at the freezing point is probably not very different from that in water. Hence $\Delta F/2$ is approximately equal to the free energy of activation $\Delta F^{\ddagger}$ for the relaxation process. The concentration of activated complexes is therefore about the same as the concentration of $H_3{}^+O$ and of O^-H ions, i.e., about 10^{-8} to 10^{-7} times the concentration of water molecules. Our results for water show that proton conductance should set in for somewhat lower frequencies, i.e., such relaxation times will correspond to free energies of activation of about 1.5 to 3.5 kcal. higher than that for the relaxation times measured in ice. Debye has pointed out that the observed polarization with an applied

TABLE III.

T (abs.)	273	291	298	323	348	373	401	429
H	222.5	314	350	465	565	644	722	777
Na	26	43.5	50.9	82	116	155	203	249
H−Na	196.5	270.5	299	383	449	489	519	528
$RT\frac{d\ln k^{\ddagger}}{dT}$ cal.	2822	2482	1907	1430	886	636	211	
$\Delta F^{\ddagger}-RT\ln B$ cal.	1508	1431	1409	1352	1346	1389	1435	1521

[19] J. G. Kirkwood, J. Chem. Phys. **4**, 539 (1936); Lars Onsager, J. Am. Chem. Soc. **58**, 1486 (1936); Hans Mueller, Phys. Rev. **50**, 547 (1936).

[20] Errera, J. de phys. **5**, 304 (1924); Smyth and Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932). We also want to express our appreciation for the opportunity of discussion with Professor Smyth.

[21] E. J. Murphy, Trans. Electrochem. Soc. **65**, 133 (1934).

[22] Debye, *Polar Molecules* (Chemical Catalog Co., 1929).

potential of 1 volt/cm could be accounted for by one molecule in 5×10^6 orienting. If the ions present in H_2O migrated toward the electrodes until space charge stopped them (even if there were no discharge) the apparent polarization and conductance would far exceed that observed. This is clear since if pairs of ions moved one space further apart under unit potential gradient it would approximately account for the observed polarization.

Since the observed polarization in ice is probably due to rotation, and therefore faster than proton transfer, our assumption that in water proton migration is slower than rotation and therefore is rate determining seems reasonable. This argument is far from conclusive, however. Thus the fact that H_2O in ice rotates with a lower free energy than the observed value for conductance in water does not, of course, prove that H_3O^+ ions in water also rotate with a lower free energy of activation. As a matter of fact, Wannier[17a] from a comparison of his quantum-mechanical calculations with the experiments on conductance concludes that rotation is slowest. Whichever process is the slow one our conclusion that the free energy of activation for proton transfer is not in excess of about 3.5 kcal. is a necessary one.

Having considered the simplest reaction involving the breaking of a hydrogen bond we next consider another type—the vaporization of water. Since the activated complex is simply the vapor molecule, the rate of vaporization from a square centimeter of surface in moles per second is given by the expression $\kappa C_g(2\pi mkT)^{\frac{1}{2}}$, where κ is the transmission coefficient, C_g is the equilibrium vapor concentration in moles per cc, and $(2\pi mkT)^{\frac{1}{2}}$ is the average velocity normal to the surface.[22a] The only novel feature in this calculation is the partition function used for the liquid water,

$$F_l=\frac{(2\pi m_l kT)^{\frac{3}{2}}}{h^3}V_f(1-\exp(-500hc/kT))^{-1}\times(1-\exp(-167hc/kT))^{-2}F_{\text{vib}}. \quad (26)$$

Here m_l is the effective translational free mass, V_f is the free volume of the liquid and c is the velocity of light. The frequency 500 cm^{-1} is Cartwright's observed value[23] for the oscillation in which only hydrogen atoms move, interpreting his results in accordance with the model of Bernal and Fowler. He finds the corresponding frequency in D_2O to be nearly $500\times2^{-\frac{1}{2}}$. The oscillation 167 cm^{-1} is also his observed value for the other pair of approximately equal oscillational frequencies in which the effective mass is about that of the oxygen. He found this frequency to be not appreciably changed in heavy water. In our partition function for heavy water we take these frequencies to be $167\times(18/20)^{\frac{1}{2}}$ cm^{-1}. Because of the way the water is constrained to oscillate by its neighbors the effective translational mass is considerably less than 18. The free volume is taken to be $V_f=bT^n$, where n is found to be 5.029 from the condition that $(d/dT)(RT^2d\ln F_l/dT)=18.0$, the molal heat capacity of water. For D_2O we use 18.32 for the heat capacity per mole. This gives $n=5.024$. The value 18.32 was obtained by finding ΔC_p for liquid over vapor from the vapor pressure measurements of Miles and Menzies[24] and adding this to C_p for gaseous D_2O assumed equal to Lewis and Randall's value for H_2O vapor.[25] Brown, Barnes and Maass[26] find by direct measurement a heat capacity for D_2O of 20. We are unable to reconcile these two results. The partition function

[22a] K. F. Herzfeld, J. Chem. Phys. **3**, 319 (1935).

[23] Cartwright, Phys. Rev. **49**, 470 (1936).

[24] Miles and Menzies, J. Am. Chem. Soc. **58**, 1067 (1936).

[25] Lewis and Randall, *Thermodynamics* (McGraw-Hill, New York, 1923), p. 80.

[26] Brown, Barnes and Maass, Can. J. Research **12**, 699 (1925); **13B**, 167 (1935).

TABLE IV.

T (abs.)	272.3	270.5	269.3	265.7	264.7	261.3	252.6	240.6	227.3	266.0	261.1	227.3
$\tau\times10^5$	2.06	2.31	2.69	3.74	3.90	6.27	18.9	66.4	434	3.47	5.45	208
$T_1\times10^7$	8.65	9.49	10.5	15.5	16.1	25.3	76.2	268	1750	19.3	23.2	964
$\Delta F^\ddagger$	8390	8390	8400	8490	8470	8620	8850	9010	9340	8610	8350	9070

for the gas is

$$F_g=\frac{(2\pi mkT)^{\frac{3}{2}}V}{h^3}\,\frac{8\pi^2(8\pi^3ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{2h^3}\times F_{\text{vib}}\exp(-E_0/kT). \quad (27)$$

$F_g=F_l$ so that we obtain for the concentration of light or heavy water in the gas:

$$C_g=\frac{1}{V}=\frac{p}{RT}=\frac{m^{\frac{3}{2}}8\pi^2(8\pi^3ABC)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{2h^3(m_l^{\frac{1}{2}}b)T^n\prod_{i=1}^{3}(1-\exp(-h\gamma_i/kT)^{-1}e}\times\exp(-E_0/kT), \quad (28)$$

where p is the vapor pressure. We use the moments for light and heavy water tabulated by Topley and Eyring.[27] Two quantities remain to be determined from the vapor pressures. These are E_0 and $(m_l^{\frac{1}{2}}b)$. For H_2O these values are, respectively, 13042. calories and 8.43×10^{-14}, and for D_2O 13426.calories and 1.352×10^{-13}. Here m_l and therefore m are in atomic units. Newton and Eyring[28] find that for a variety of gases the intermediate value of b is about 10^{-14}, so that an effective translational mass for H_2O and D_2O of around 10 and 14, respectively, is reasonable. Table V shows the agreement between the experimental and the calculated vapor pressures. The experimental values for D_2O are those given by Miles and Menzies.[24] Since we have not taken account of holes as seems necessary to understand critical phenomena our equation must necessarily give too low vapor pressures at high temperatures.[29]

The abnormally large value of the entropy of vaporization of water arises from the fact that, unlike many liquids, the molecules are unable to rotate freely because of hydrogen bonds. The vapor pressure is about six times as large as for a normal liquid with the same heat of vaporization, and of course this appears as a correspondingly large value for $\Delta S^\ddagger$ in the expression for the rate of evaporation.

[27] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).
[28] Newton and Eyring, Trans. Faraday Soc. In press.
[29] Eyring, J. Chem. Phys. **4**, 283 (1936).

TABLE V.

T°C		0	20	40	60	80	100	110	140
H_2O	obs.	4.58	17.54	55.3	149.4	355.1	760	1074.6	2710.9
	calc.	4.596	17.58	55.65	150.3	356.9	760.4	1070.5	2708.3
D_2O	obs.		15.06	49.13	136.4	331.6	722.3	1028.9	2640.4
	calc.		15.10	49.36	136.9	332.5	723.9	1026.4	2633.4

We now consider as our final example of a reaction with a really abnormal entropy of activation the denaturation of proteins. Such reactions have been discussed recently by Anson,[30] Mirsky and Pauling,[31] and by Wrinch.[31a]

The results for the rate of denaturation of hemoglobin and of egg albumin, both of which proceed unimolecularly are presented in a comprehensive survey of the subject by Chick and Martin.[32] Both are first order with respect to the proteins and from their results the following tables have been prepared.

Here the specific reaction rate is expressed in reciprocal seconds.

$$\Delta F^\ddagger=-RT\ln k'+RT\ln(kT/h)$$

$$\Delta H^\ddagger=-T^2\frac{d}{dT}\left(\frac{\Delta F^\ddagger}{T}\right)$$

and $$\Delta S^\ddagger=\frac{(\Delta H^\ddagger-\Delta F^\ddagger)}{T}.$$

The steric factor is $\exp\Delta S^\ddagger/R$. Clearly the activated complex possesses enormously greater randomness than does the original molecule. This must be due to the breaking of many bonds or the opening of rings or both.

The denatured molecule as well as the activated complex has a much greater entropy than the native protein as is shown by the equilibrium results of Anson and Mirsky on tripsin.[33] Thus their experimental results yield for the reaction native tripsin→denatured at 45° the values $\Delta F=-190$ cal.; $\Delta H=-67{,}600$; $\Delta S=213$ e.u.

[30] Anson, *The Chemistry of Proteins*, Chap. IX, edited by C. L. A. Schmidt.
[31] Mirsky and Pauling, Proc. Nat. Acad. Sci. **22**, 439 (1936).
[31a] D. M. Wrinch, Nature **137**, 411; **138**, 241, 651 (1936).
[32] Chick and Martin, *Kolloid chemische Beihefte* V, 49 (1913).
[33] Anson and Mirsky, J. Gen. Physiology **17**, 393 (1934).

TABLE VI. *Hemoglobin.*

T (abs.)	k'	$\Delta F^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	STERIC FACTOR
340.7	1.23×10^{-3}	24,700	58,000	98	1.89×10^{21}
338.7	7.33×10^{-4}	24,900	58,700	100	5.14×10^{21}
335.7	3.17×10^{-4}	25,300	60,300	105	6.25×10^{22}
333.1	1.55×10^{-4}	25,600	60,400	105	6.25×10^{22}
		Egg Albumin			
344.2	1.18×10^{-4}	26,600	135,800	317	6.66×10^{68}
346.1	4.41×10^{-4}	25,850	140,900	332	1.20×10^{72}
349.4	25.4×10^{-4}	24,880	128,100	295	1.11×10^{64}

Here the entropy change for the equilibrium falls in between the two previous values for the activated complexes. Unfortunately there are no data on the equilibrium and the reaction rate for the same reaction. One other well established fact is that acid and alkali affect both the equilibria and rates profoundly and this effect is usually to lessen ΔF, ΔH and ΔS each in much the same way as it affects the three corresponding rate quantities.

Mirsky and Pauling's suggestion that denaturation involves the breaking of hydrogen bonds provides a reasonable picture of the rate process. Let us assume that the 60,000 calories for $\Delta H^{\ddagger}$ in hemoglobin comes from breaking 12 hydrogen bonds of 5000 calories each. If these are between an amino and a carboxyl group then since there is only an oscillation of these groups before the bond rupture while there is rotation afterwards we should expect an increase in entropy. The rotational entropies of an amino and carboxyl group are 4.1 and 7.4 e.u. respectively or 11.5 for the sum. Twelve such pairs would give an entropy of 138 e.u. Before comparing this with the observed 100 e.u. of activation we should subtract something for the oscillational entropy of the groups before rupture and add something for the increased freedom given the other groups. All we can say then is that the increase in entropy seems quite reasonable on the basis of the hydrogen bond mechanism. The same calculation for egg albumin gives 312 e.u. to be compared with 317 at 344.2° (abs.) with similar results at the other two temperatures. In estimating the entropy we have assumed the amino and carboxyl groups in the activated complex stage are unable to form new hydrogen bonds with water. In solutions containing acid, alkali or urea, however, such bonds probably do form causing $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to drop greatly in such a way as to largely compensate each other and so give only moderate decreases in $\Delta F^{\ddagger}$ as is observed.

The results on the heat and entropy of activation do not provide a basis for a decision between the hydrogen bond theory and the cyclization theories of Dr. Wrinch providing the latter bonds are not much stronger than the hydrogen bonds. The only requirement is that the bonds broken in denaturation are such as to provide a degree of randomness unusual in chemical reactions and more nearly comparable with the breaking of bonds three or four times as strong as those broken in the melting of ice.

In previous papers a steric factor of about 10^{-6} for the unimolecular reaction by which a hexyl radical closes a five-membered ring simultaneously expelling a CH_3 group has been calculated and compared with experiment.[2a] (See also reference 6 for additional examples.) In denaturation we have a factor acting in the opposite direction making the reaction abnormally rapid by a factor of about 10^{22} and 10^{70}, respectively. The activated complex theory provides a means of understanding these and of estimating the factor to be expected in other cases. The problems of reaction rates are, in fact, principally those already met in equilibrium problems, so that methods or information useful in one field have an obvious application in the other. Each peculiar type of equilibrium is apt to be exhibited somewhere as an equally peculiar reaction rate.

We want to thank Dr. Anson for many helpful discussions on denaturation.

The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites

VIII. The Decomposition of Ethyl and *n*-Propyl Nitrites at Low Pressures Together with a General Discussion of the Results for the Entire Series

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The kinetics of the decomposition of ethyl and *n*-propyl nitrites have been investigated at low pressures. The results, together with those for the other members of the nitrite series, are discussed from the point of view of the Kassel theory. Attention is focused particularly on the effect of increasing molecular complexity as one ascends an homologous series, since the nitrites furnish an ideal series for such a discussion. It is concluded that the Kassel theory furnishes a complete explanation of the facts insofar as the effect of pressure on the rate is concerned. On the other hand, there is no satisfactory quantitative explanation of the increase in the high pressure rate with increasing molecular complexity. The factors which might contribute to such an increase are discussed, and it is concluded that the main factor is probably a progressive change in binding energy as one ascends an homologous series.

Introduction

CONSIDERABLE attention has been directed in recent years to the study of unimolecular reactions. It now appears that the initial step in nearly all organic decompositions is unimolecular in character, and that the whole question of the stability of gaseous organic substances is virtually reduced to the determination of the unimolecular rate constants.

The variation of the constants A and E in the expression for the rate constant,

$$k = Ae^{-E/RT},$$

as one passes from one member to the next in an homologous series has been the subject of frequent investigation during the past few years. In general a number of criticisms may be directed against the series of compounds previously investigated. In the case of the aliphatic ethers the mode of decomposition varies from member to member of the series, and in any case recent work seems to indicate that the decompositions are much more complex than appeared at first sight.[1] The azo compounds[2] in addition to possessing a somewhat complex decomposition mechanism, are further complicated by the presence of a side reaction of increasing prominence as one goes up the series. The esters and paraldehydes[3] are rather more satisfactory for comparative purposes. Here, too, however, while the reactions are definitely comparable, they involve a mechanism in which two bonds are broken and one other bond is converted from single to double. The physical significance of the energy of activation is therefore somewhat obscured.

Recently a series of investigations on the decomposition of the gaseous alkyl nitrites has been made in this laboratory.[4] It appears that the primary and rate determining step in all cases is

$$\mathrm{RONO} = \mathrm{RO} + \mathrm{NO}.^{5}$$

Hence only one bond is broken in the reaction, and it is the same bond for every member of the series. The reactions have also been shown to be homogeneous and unimolecular over a wide pressure range.

The present communication deals with an investigation of the decomposition of ethyl and *n*-propyl nitrites at low pressures, together with a general discussion of the results for the entire series.

[1] Rice and Sickman, J. Am. Chem. Soc. **56**, 1444 (1934); Steacie and Solomon, J. Chem. Phys. **2**, 503 (1934); Steacie, Hatcher and Rosenberg, ibid. **4**, 220 (1936).
[2] Ramsperger, J. Am. Chem. Soc. **49**, 912, 1495 (1927); **50**, 714 (1928); **51**, 2134 (1929).
[3] Coffin, Can. J. Research **5**, 636 (1931); **6**, 417 (1932); **7**, 75 (1932); **9**, 603 (1933).
[4] Steacie and Shaw, J. Chem. Phys. **2**, 345 (1934); **3**, 344 (1935); Proc. Roy. Soc. (London) **A146**, 388 (1934); **A151**, 685 (1935); Steacie and Calder, J. Chem. Phys. **4**, 96 (1936); Steacie and Rosenberg, ibid. **4**, 223 (1936); Steacie and Smith, ibid. **4**, 504 (1936).
[5] Rice and Rodowskas, J. Am. Chem. Soc. **57**, 350 (1935).

Experimental

Ethyl nitrite was prepared and purified under reduced pressure as previously described. It was stored as a liquid in a bulb at −80°C during the investigation.

The reaction was carried out in a constant volume system, and was followed by observing changes in pressure. The reaction vessels were two Pyrex bulbs of about one liter capacity. One of them possessed a surface volume ratio of about 0.6 cm^{-1}: the other was packed with short lengths of Pyrex tubing, giving a surface volume ratio of about 3.0 cm^{-1}. The reaction vessel was immersed in an electrically heated oil bath, the temperature of which could be maintained constant to within 0.2° by manual control. Temperatures were measured by means of standard mercury thermometers.

In the higher pressure range the apparatus was constructed of 3/16-inch tubing, with stopcock connections lubricated with Apiezon *N* grease. Pressure changes were followed with a differential mercury manometer, and readings could be taken at very frequent intervals. (See Table I.) At lower pressures wider tubing was employed, all stopcocks were replaced by mercury seals, and a set of McLeod gauges was substituted for the manometer. These gauges were of very small volume to reduce to a minimum dead space fluctuations when they were cut in and out of the system. Actually each gauge comprised less than one percent of the total volume of the reacting system and about ten percent of the total dead space.

A number of control runs were made to check the time necessary for the establishment of pressure equilibrium, etc. The system could be consistently evacuated to about 10^{-5} cm by means of a two-stage steel Leybold diffusion pump, and no appreciable pressure change occurred when the system was cut off from the pump and allowed to stand for a time comparable with the duration of a normal experiment. On a few occasions the system was flushed out with nitrogen before making a run, but this procedure had no effect upon the result. During a number of runs a piece of gold foil was inserted between the reaction vessel and the mercury surfaces of the gauge and cutoff, but this also had no observable effect on the progress of the reaction. It was also shown that heating the gauges and connecting tubing to 90°C during runs had no effect on the rate of reaction or upon the pressure increase at completion. Various samples of ethyl nitrite were used, and these gave identical results.

In carrying out an experiment the reaction system was first cut off from the pump. A suitable amount of ethyl nitrite vapor was then expanded into the reaction system by opening the stopcock or mercury cutoff leading to the reservoir for seven seconds. The initial pressure reading was made eight seconds later, and further readings were taken at intervals until the pressure ceased to change. In runs made with a McLeod gauge, the gauge was kept connected to the reaction system between observations, and was cut off only when readings were being taken. It was, of course, impossible to make readings as frequently with a McLeod gauge as with a manometer.

Propyl nitrite was prepared and stored in a manner analogous to that of ethyl nitrite. Several samples were prepared at normal and at reduced pressures, and their purity was checked by boiling point determinations. All runs were made at pressures below 3 cm, using McLeod gauges. To eliminate the possibility of the condensation of the products of reaction, all experi-

Table I. *Complete data for typical runs with ethyl nitrite.* Run No. 9. 494.6°K. Initial pressure = 10.9 cm. Pressure measurements made with a manometer.

Time (sec.)	ΔP (cm)	k ($sec.^{-1}$)	Time (sec.)	ΔP (cm)	k ($sec.^{-1}$)
0	0.0	——	300	5.2	0.0029
15	0.3	0.0023	360	5.7	0.0028
30	0.6	0.0025	420	6.15	0.0028
45	1.0	0.0026	480	6.6	0.0028
60	1.35	0.0028	600	7.2	0.0028
90	2.0	0.0029	840	8.0	0.0028
120	2.65	0.0028	1500	8.65	0.0024
180	3.60	0.0029	2100	8.85	0.0025
240	4.5	0.0029	3000	8.9	——

Graphically $T_{25} = 102$ sec., $T_{50} = 235$ sec.

Run No. 84. 494.6°K. Initial pressure = 0.0422 cm. Pressure measurements made with a McLeod gauge.

0	0.0	——	1800	0.0304	0.00131
300	0.0130	0.00142	2400	0.0376	——
600	0.0210	0.00136	3000	0.0376	——
900	0.0269	0.00139	3600	0.0376	——
1200	0.0304	0.00138			

Graphically $T_{25} = 210$ sec., $T_{50} = 510$ sec.

ments were made with the gauges thermostated at 100°C and with the connecting tubing heated electrically to the same temperature. Runs made with the packed reaction vessel did not deviate appreciably from those with the empty vessel. In spite of all precautions, the experiments with propyl nitrite were much less reproducible than those with ethyl nitrite. There seemed to be no apparent explanation of this fact.

Experimental Results

All runs were carried to completion. The times for 50 percent, and 25 percent, of the total pressure increase to occur were obtained graphically, and were used as a measure of the rate of reaction.

I. Ethyl nitrite

In all about 100 runs were made at three different temperatures. Complete data for two runs in the empty reaction vessel are given in Table I. The data for all runs are given in Figs. 1 and 2, in the form of $\log P - \log 10^4/T_{50}$ and $\log P - \log 10^4/T_{25}$ graphs, and the data for a series of representative runs are given in Table II.

The mean pressure increase for all runs was 84.8 percent, in excellent agreement with Steacie and Shaw's high pressure value of 86 percent. The final pressure was quite sharply defined, and showed no tendency to fall off slowly as was reported in the case of methyl nitrite.

For the sake of comparison, Steacie and Shaw's high pressure rates are plotted in Fig. 1 (indicated by double circles). The agreement is remarkably good. It may be observed that Steacie and Calder reported rates slightly lower than those of Steacie and Shaw in the case of methyl nitrite, and this is also the case here at the one temperature at which the difference was appreciable.

Runs made with the packed reaction vessel are indicated by solid circles in Fig. 1. It is obvious that the reaction is not appreciably heterogeneous down to pressures of 10^{-2} cm.

II. *n*-Propyl nitrite

The experiments with propyl nitrite were all made at 483.6°K. Considerable difficulty was experienced in obtaining reproducible data, and,

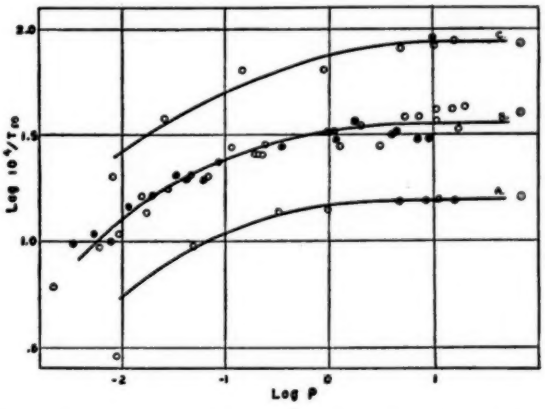

FIG. 1. The variation of T_{50} with pressure for ethyl nitrite.

as Table III and Fig. 3 indicate, some uncertainty attaches to this work. The results are, however, accurate enough to establish fairly definitely the pressure at which the rate begins to fall off appreciably. As may be seen from Fig. 3, the agreement with the results of Steacie and Shaw is well within the experimental error. Packing the reaction vessel had no apparent effect on the results.

Discussion

The most important characteristic of a unimolecular reaction is the falling off in rate at low pressures. As predicted by the theory, ethyl nitrite maintains its high pressure rate down to lower pressures than does methyl nitrite, and the still more complex propyl nitrite maintains it to even lower pressures.

We shall now proceed to a discussion of the effect of pressure on the rate for the alkyl nitrites from the standpoint of the Kassel theory.[6] Kassel assumes that if a molecule has j quanta divided among s oscillators it will react when m quanta are localized in a particular bond. He then gets directly for the rate of reaction at high pressures

$$k_\infty = A(1-e^{-h\nu/kT})^s \sum_{j=m}^{\infty} \binom{j+s-1}{s-1} \times \frac{j!(j-m+s-1)!}{(j-m)!(j+s-1)!} e^{-jh\nu/kT}, \quad (1)$$

[6] Kassel, *Kinetics of Homogeneous Gas Reactions* (New York, 1932), p. 96 *et seq.*

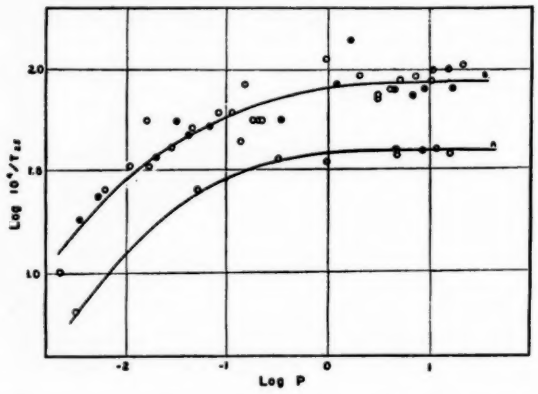

FIG. 2. The variation of T_{25} with pressure for ethyl nitrite.

which, on carrying out the summation reduces to

$$k_\infty = Ae^{-mh\nu/kT}. \quad (2)$$

Here A has the general character of the reciprocal of a relaxation time, and ν is the frequency of the oscillators, all of which are, for simplicity, assumed to be identical.

At low pressures we must consider the number of collisions, etc., and for k, the rate at low pressures, we get

$$k = k_\infty(1-e^{-h\nu/kT})^s \sum_{j=m}^{\infty} \frac{\binom{j-m+s-1}{j-m} e^{-(j-m)h\nu/kT}}{1+\frac{A}{aN}\frac{(j-m+s-1)!j!}{(j-m)!(s-1)!}}, \quad (3)$$

where a, the collision factor, $=4(\pi kT/m_0)^{\frac{1}{2}}\cdot\sigma^2$, m_0 is the molecular weight, and σ the molecular diameter.

In applying this relationship, we put $mh\nu N_0 = E$, where E is the energy of activation, and N_0 is Avogadro's number. The value of ν is adjusted so as to give agreement between the observed and calculated values of k/k_∞ at various pressures, although, of course, it must be roughly consistent with known vibrational frequencies of the molecule. The number of effective oscillators in the molecule, s, is taken as the total number ($3n-6$, where n is the number of atoms) less the number of C–H bonds, since these possess too high a frequency to be thermally excited at the temperatures under consideration.

As a result of the series of investigations on the decomposition of the alkyl nitrites, we now have available for the first time data for an homologous series of compounds in which (a) we are sure that exactly the same primary reaction is taking place in all cases, and (b) the substances are simple enough to enable us to determine the falling off in rate at low pressures for several members of the series.

For what we might call an ideal series of homologues, the same bond would be broken in every case, and the bond strength would be the same throughout the series. A methyl derivative possessing definite values of m and s should be followed by an ethyl derivative with $m_{et}=m_{me}$, and $s_{et}=s_{me}+7$, and a propyl derivative with $m_{pr}=m_{me}$, and $s_{pr}=s_{me}+14$, etc. Furthermore E, since it is equal to $N_0mh\nu$, should be constant throughout the series. Hence, from Eq. (2), k_∞ should be the same for all members of the

TABLE II. *Summarized data for representative runs with ethyl nitrite.*

P_0 (cm)	Final % ΔP	T_{25} (sec.)	T_{50} (sec.)	P_0 (cm)	Final % ΔP	T_{25} (sec.)	T_{50} (sec.)
Manometer 494.6°K							
21.25	85.1	96	230	4.15	87.9	126	312
15.3	83.7	102	235	2.05	110.0	108	285
10.6	83.9	102	235	0.95	106.0	90	300
7.3	84.9	108	255				
McLeod Gauge 494.6°K							
1.12	74.2	135	300	0.0153	80.4	180	630
0.205	78.5	180	390	0.0093	89.1	420	930
0.146	74.4	120	270	0.0061	81.8	390	1080
0.0835	73.9	165	420	0.00207	86.6	1020	1650
0.0283	84.1	240	570				
Packed Bulb 494.6°K							
17.1	84.8	126	300	0.0332	90.3	180	480
6.9	92.1	135	330	0.00536	84.0	420	930
4.45	96.6	126	300	0.00343	84.0	540	1020
0.344	83.7	180	360				
483.6°K							
16.3	87.1	258	642	0.321	79.0	276	734
8.5	88.2	252	645	0.0506	72.7	390	1050
4.85	94.8	258	642	0.0032	103	1530	3510
0.996	78.9	285	720				
505.0°K							
15.5	86.1	—	114	0.146	70.0	—	72
4.8	82.3	—	123	0.0257	75.1	—	125
0.906	71.2	—	90	0.0083	84.3	—	228

series, provided that A does not vary. This latter probability is discussed later.

The results obtained for the high pressure rate constants of the nitrite decompositions are:

$$k_{\text{methyl}} = 1.84\times10^{13}\, e^{-36400/RT} \text{ sec.}^{-1},$$
$$k_{\text{ethyl}} = 1.39\times10^{14}\, e^{-37700/RT},$$
$$k_{\text{propyl}} = 2.75\times10^{14}\, e^{-37650/RT},$$
$$k_{\text{iso-propyl}} = 1.26\times10^{14}\, e^{-37000/RT},$$
$$k_{\text{butyl}} = 3.02\times10^{14}\, e^{-37000/RT}.$$

The variations in E are within the experimental error, but their interdependence with the non-exponential term obscures any regularities in the rates. For the moment let us arbitrarily put $E=37000$ calories per gram mole for all the reactions, and recalculate A. We get

Substance	A	A/A_{me}
Methyl nitrite	0.33×10^{14}	(1.0)
Ethyl nitrite	0.65×10^{14}	2.0
n-propyl nitrite	1.35×10^{14}	4.1
iso-propyl nitrite	1.26×10^{14}	3.8
n-butyl nitrite	3.02×10^{14}	9.1

In other words the rate approximately doubles for each added CH_2 group. This is in general agreement with Coffin's results. It may also be noted that within the experimental error the rates for *n*-propyl and iso-propyl nitrites are identical.

We now come to the consideration of the low pressure rates. Fig. 4 gives the experimental curve for methyl nitrite together with the predictions of the Kassel theory for $\sigma=3.0\times10^{-8}$ cm, $s=12$, $m=13$ and 14, and a temperature of 494.3°K. The value used for A in these calculations was one-half the experimental value, since it appears certain that in the nitrite decompositions two molecules disappear for each

TABLE III. *Summarized data for experiments with propyl nitrite. Temperature = 483.6°K.*

P_0 (cm)	Final % ΔP	T_{50} (sec.)	P_0 (cm)	Final % ΔP	T_{50} (sec.)
1.066	70.5	240	0.121	77	270
0.709	68	285	0.116	78	315
0.314	72.5	360	0.0920	90	270
0.275	94	240	0.0420	83	555
0.210	66	270	0.0415	95	270
0.182	89	270	0.0395	97	360
0.125	88	270	0.0320	106	420

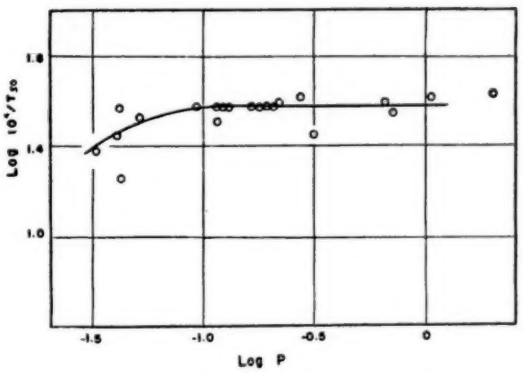

FIG. 3. The variation of T_{50} with pressure for propyl nitrite.

elementary act.[5] The agreement of theory with experiment seems quite satisfactory with m equal to either 13 or 14.

Fig. 5 gives similar results for ethyl nitrite, s being taken as 19, and other factors as shown in the figure. It is seen that excellent agreement is obtained if we use the same values for m and σ as were used with methyl nitrite.

A similar calculation for propyl nitrite, using $s=26$ and other factors as with methyl nitrite, shows that the falling off in rate should not be appreciable above 0.1 cm. This is consistent with the experimental results given in Fig. 3.

It may therefore be concluded that the Kassel theory gives excellent agreement with the experimental facts. In this connection it should be emphasized that all adjustable parameters are exhausted in fitting the theory to the results for methyl nitrite, and that there are no further opportunities for adjustment of the theoretical values for ethyl and propyl nitrites. The nitrites, therefore, approximate very closely to the ideal homologous series discussed above. The theory, however, offers no explanation of the slight but regular increase in the high pressure rates as one ascends the series.

In looking for an explanation of this effect, it is obvious in the first place that the diameter and mass of the molecule, steric effects, etc. can have no effect since they all vanish in the expression for the high pressure rate. A variation in the proportionality factor, A, would account for the observed effect. While the significance of A is rather hazy,[7] it has the general meaning of the

[7] See Kassel, Chem. Rev. **10**, 11 (1932).

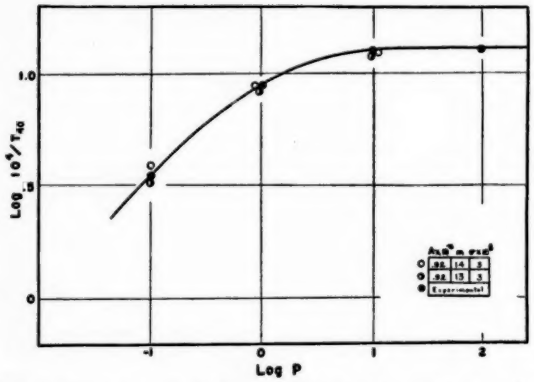

FIG. 4. Comparison of theory with experiment for methyl nitrite.

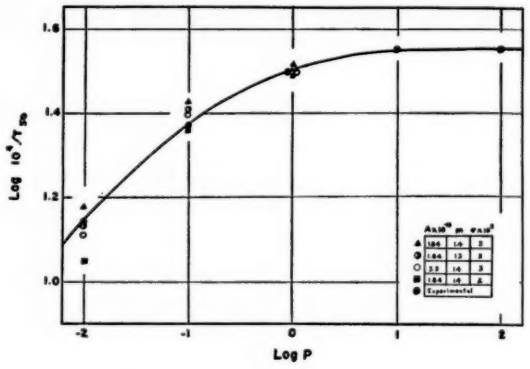

FIG. 5. Comparison of theory with experiment for ethyl nitrite.

reciprocal of a relaxation time. It would therefore be expected that it would diminish with increasing molecular complexity, which is the reverse of the experimental observations. It therefore seems unlikely that the explanation of the facts is to be found here.

There is evidence that bond strengths may diminish as we ascend an homologous series. Thus Ramsperger has reported a progressive decrease in the activation energies of the azo compounds. Rice and Johnson[8] in discussing the strength of the C−C bond in saturated hydrocarbons report a progressive decrease in the energy of activation for the split into free radicals with increasing molecular weight. There is, of course, considerable doubt regarding the relationship between the low temperature decomposition and the free radical decomposition of the saturated hydrocarbons, but it appears almost certain that the primary step in the nitrite decompositions is a direct split into radicals, and is therefore directly comparable with Rice and Johnson's work.

It seems therefore that the most probable explanation of the increase in the high pressure rate as one ascends the nitrite series is to ascribe it to small changes in E, A probably remaining roughly constant. Since $E=N_0mh\nu$, it follows that either m or ν must change. A change in m of 1 would correspond to a change in E of 2580 calories, while a change of 600 calories from member to member is all that is required to bring the high pressure rates into agreement. Of course the "quanta" involved are highly artificial in character and fractional changes might be permitted. The most simple and logical assumption, however, is that there is a slight progressive decrease in ν as one ascends the series. Assuming $m=14$ for methyl nitrite in the above calculations is equivalent to putting $h\nu=2580$ calories per mole, whence $\nu=910$ cm^{-1}. All that would be required to bring the high pressure rates into line would be a decrease in ν of 15 cm^{-1} from member to member. Such a decrease is by no means unreasonable from the point of view of molecular structure.

Rice and Gershinowitz[9] on the basis of the "freezing out" of degrees of freedom, have recently calculated the A factors for methyl and ethyl nitrites. They find the same value for both. The calculation, however, is based on the assumption of the same frequency in both cases for the bond which is about to break, and a small change in this frequency from member to member of the series could materially change the A factor.

It follows that the whole situation is complicated in that a small change in the frequency of the pertinent bond may be expected to change both A and E. At the moment there is no theory sufficiently detailed to predict accurately what will happen as one ascends an homologous series, but qualitatively at least it appears that the assumption of small changes in binding strengths is a sufficient explanation of the facts.

[8] J. Am. Chem. Soc. **56**, 214 (1934).

[9] J. Chem. Phys. **3**, 479 (1935).

A Study of Long Chain Organic Compounds by Electron Diffraction

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(Received November 28, 1936)

A layer of lard deposited upon a metal surface gives an electron diffraction pattern consisting of segments of diffuse inclined bands. These arise from line gratings made up of long hydrocarbon chains. The mean inclination of the axes of these chains to the surface normal is calculated to be 27°, and the separation of carbon atoms 2.50A. The saturated glyceride, tri-stearin, yields a diffraction pattern of diffuse bands parallel to the surface, unlike the diffraction pattern from lard, although the latter is predominantly a mixture of glycerides. We believe that the inclination of the long hydrocarbon chains in lard is due to lack of saturation, although this hypothesis has not been tested. Diffraction patterns from stearic acid deposited upon a metal surface also contain inclined bands. These are relatively well defined, and have inclinations which differ from one sample to another. This variation is attributed to the existence of large crystals the c axes of which are differently inclined to the plane of incidence. We calculate that this axis is always inclined 33° to the surface normal. A similar investigation of methyl stearate yields the angle 25°. For both stearic acid and methyl stearate the separation between diffraction bands corresponds to the atomic spacing 2.50A. This is in good agreement with the known distance between alternate carbon atoms in a zigzag hydrocarbon chain.

SEVERAL experimenters have examined long chain organic compounds by electron diffraction.[1] The first to report an investigation of this kind were Thomson and Murison who studied long chain greases of the paraffin type deposited on metal surfaces. They, as well as later workers, obtained diffraction patterns consisting of several diffuse parallel and equally spaced bands on which appear a few fuzzy spots. These patterns are attributed to extremely imperfect crystals containing long hydrocarbon chains standing approximately normal to the supporting surface.

In general the materials studied in this manner have been mixtures of saturated single chain compounds containing carbon and hydrogen only. Although crystallographic data on such compounds are not extensive, they indicate that these often, if not always, crystallize in the orthorhombic system with the axis of the long chain parallel with one of the crystallographic axes. The observations by electron diffraction have been consistent with this type of structure, and from these observations it is deduced that paraffin type hydrocarbon compounds orient themselves upon a metal surface with the two short crystal axes lying in the plane of the surface.

[1] The earliest papers are: Thomson and Murison, Nature **131**, 237 (1933); Nelson, Phys. Rev. **44**, 717 (1933); Murison, Phil. Mag. **17**, 201 (1934).

Lard

We decided to study an entirely different type of greasy compound. For this we chose commercial lard as a typical grease mixture of animal origin. Samples of lard were prepared on blocks of polycrystalline nickel which had been carefully polished and freshly cleaned. Diffraction patterns were obtained from these by scattering high speed electrons at very small glancing angles. Essentially similar patterns were found when lard was deposited by evaporation from benzene solution, when it was simply rubbed upon the metal surface, and when it was fused and allowed to flow freely. In still another experiment lard was deposited upon the naturally formed face of

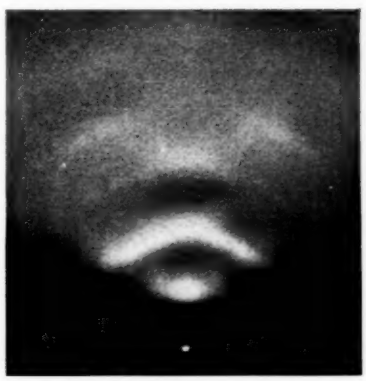
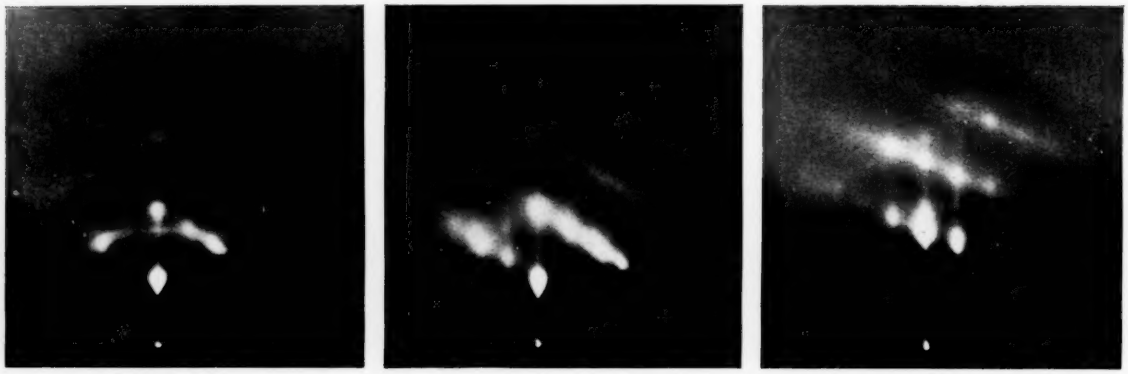


FIG. 1. Electron diffraction pattern from a layer of lard upon a block of polished nickel. ($\lambda = 0.051$A.)



A B C

FIG. 2. Diffraction patterns from stearic acid. ($\lambda = 0.051$A.)

a single crystal of carborundum, and in this case also the pattern was like those found earlier.

A typical diffraction pattern obtained from lard is shown in Fig. 1. The diffuse smears of this figure are portions of two sets of parallel bands, the members of each set being equally spaced and inclined at angles of about 27° to the plane of the specimen surface. Except for this inclination the features of Fig. 1 are rather like those observed for paraffin, and we interpret them in an analogous manner. The two sets of bands correspond to hydrocarbon chains which are inclined to the surface normal by angles within a range about 27° but are otherwise unrelated.

To see how this comes about we consider first the diffraction effect of a single chain of carbon atoms. We designate by d the separation of atoms measured along the direction of the chain, by α the angular inclination of the chain to the surface normal, and by φ the azimuth of the chain measured from the plane of incidence. This chain of carbon atoms would give rise to diffraction cones intersecting the photographic plate in lines approximately straight, parallel and equally spaced.[2] These lines are described by the equation

$$y = n\frac{L\lambda}{d\cos\alpha} + x\tan\alpha\sin\varphi \qquad (1)$$

where x and y are coordinates in a Cartesian system with its origin at the intersection of the primary beam with the photographic plate and its x axis parallel to the supporting surface. (λ is the electron wave-length, L the distance from specimen to photographic plate and n any whole number.)

The common slope of the lines is $dy/dx = \tan\alpha\sin\varphi$, and their intersections with the y axis are $nL\lambda/d\cos\alpha$. We note that if φ is varied while α remains fixed the lines are turned about these fixed intersections. The slopes can be varied from $-\tan\alpha$ to $+\tan\alpha$; the angles which the lines make with the x axis are varied from $-\alpha$ to $+\alpha$. As the azimuth plane of the molecule is rotated the diffraction lines sweep out symmetrical pairs of sectors of angular width 2α. If all the molecules in the diffracting material have the same value of α but are randomly disposed in azimuth these sectors will appear on the pattern. They will not be uniformly intense across their widths, but most intense at the edges and least intense at the centers.

The diffuse bands of Fig. 1 are the edges of these predicted sectors. Nevertheless only short

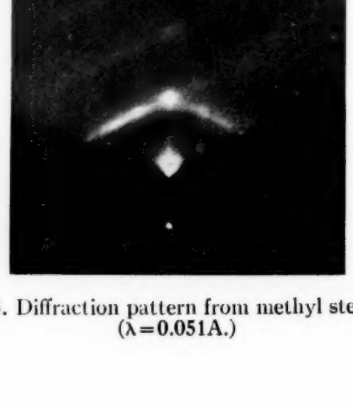


FIG. 3. Diffraction pattern from methyl stearate. ($\lambda = 0.051$A.)

[2] Except for the very special case of α near $\pi/2$ and φ near zero.

sections of the bands appear, and their behavior at the y axis is not that to be expected from the analysis just given. We must assume that α also is somewhat variable from one chain to another. From Eq. (1) one finds that, for $\varphi=\pi/2$ which is the most important case, as α varies a line will remain at a fixed distance from the origin and its inclination will remain equal to α.

We believe that the observed diffraction pattern arises from hydrocarbon chains distributed randomly in azimuth and inclined at somewhat differing angles to the surface normal. Because of the complex nature of lard and the extreme fuzziness of the features of Fig. 1 it seems unprofitable to attempt to carry the analysis further. We can, however, conclude that most of the hydrocarbon chains in lard are inclined to the surface normal by angles in the neighborhood of 27°. The separation of carbon atoms, d, can also be calculated. From Eq. (1) the distance between adjacent bands is given by

$$D=\frac{nL\lambda}{d(1-\cos^2\varphi\sin^2\alpha)^{\frac{1}{2}}}. \qquad (2)$$

As the diffuse bands represent the edges of the sectors we have $\varphi=\pi/2$, and Eq. (2) allows us to calculate $d=2.50$A.

We have investigated some of the compounds which might be in lard. As it is known to be a mixture of glycerides of long chain organic acids plus small amounts of free acids we chose to study stearic acid and tri-stearin, a glyceride of stearic acid. These compounds are not exactly typical of the constituents of lard because the chains of both are completely saturated whereas the natural product is known to contain a considerable proportion of unsaturated chains.

We have found that tri-stearin produces a diffraction pattern of straight lines lying parallel to the supporting surface, entirely unlike the pattern obtained from lard. Separations of these lines correspond again to the spacing 2.50A. Lines of even order are strong and lines of odd order weak. From this pattern we predict that the structure of tri-stearin will probably be found to be orthorhombic.

Examples of diffraction patterns from stearic acid are shown in Fig. 2. Although these exhibit inclined lines and resemble the pattern from lard in a rather striking fashion, it is known that lard contains little free acid. We were then led to test a mixture made up of tri-stearin and a small percentage of free stearic acid. This mixture gave the diffraction pattern of tri-stearin, without any observable modification due to the acid. It is interesting to note that the mixture is very different from lard mechanically. We now believe that the inclination of the long hydrocarbon chains in lard is due to lack of saturation of these chains in the acid radicals in the glycerides. This hypothesis has not been tested as we have been unable to obtain glycerides of unsaturated long chain acids which are solid at room temperature.

Stearic Acid

The diffraction patterns of Fig. 2 were produced by stearic acid deposited upon polished nickel by evaporation from benzene solution. Although these patterns exhibit fairly well defined spots characteristic of single crystals, they also show the inclined bands which are attributed to the separate molecules. We conclude that the crystals are extremely imperfect, so imperfect that diffraction patterns from the independent line gratings of separate molecules are still evident.

Microscopic examination shows that layers of stearic acid have a strong tendency to form large crystals. Differences in disposition and size of these crystals undoubtedly account for the differences between the patterns of bands in Fig. 2.

The first of these, Fig. 2*A*, resembles the lard pattern. The equal intensities and inclinations of the two sets of bands in this figure indicate that the stearic acid crystals are more or less randomly disposed in azimuth. The actual inclinations and spacings of the observed bands will then correspond to long hydrocarbon chains lying in the two azimuths normal to the primary beam. That this assumption is true is borne out by the fact that most stearic acid diffraction patterns exhibit bands having approximately the same inclination as those of Fig. 2*A*. This inclination occurs most frequently although substantially smaller inclinations are sometimes found, and even bands parallel to the surface are observed in rare cases.

The single set of bands of Fig. 2*B* has the same inclination as the two sets of Fig. 2*A*. This single set of bands corresponds to hydrocarbon chains

lying in *one* azimuth normal to the primary beam direction, or at least in azimuths within about 25° (estimated by means of Eq. (1)) of this normal position. The lack of sharpness of the features of Fig. 2*B* suggests that the pattern does, in fact, arise from many crystals the hydrocarbon chains of which are located in different azimuths. The bands of Figs. 2*A* and 2*B* yield the values $d=2.50$A and $\alpha=33°$.

The sharp features of Fig. 2*C* suggest that this pattern is produced by a single imperfect crystal. That this is true is evidenced further by the fact that the inclination of the lines of Fig. 2*C* is only 24°. From the relation $dy/dx=\tan\alpha\sin\varphi$ we can calculate the azimuth, φ, which corresponds to the slope $dy/dx=\tan 24°$ assuming, of course, the value $\alpha=33°$ obtained from Figs. 2*A* and 2*B*. This calculation yields $\varphi=45°$ (or 135°) as the azimuth of the hydrocarbon chains producing the pattern of Fig. 2*C*. If this value of φ is substituted into Eq. (2) together with $\alpha=33°$ and $d=2.50$A we obtain $D=8.6$ mm as the spacing of the lines of Fig. 2*C*. Direct measurement gives 8.5 mm. (The separations in Figs. 2*A* and 2*B*, from which the value 2.50A was calculated, are 8.0 mm.)

It is interesting to compare the angle $\alpha=33°$ and the spacing $d=2.50$A, obtained from these experiments, with the results of measurements upon single crystals of stearic acid. Müller[3] gives 2.51A as the distance between alternate carbon atoms in the zigzag chain of the acid and, for the β modification, he has found the angle between the *c* axis and the normal to the basal plane to be 26° 22′. For the α modification[4] this angle is reported to be 39° 10′. New and, as yet, unpublished electron diffraction measurements[5] by us upon single crystals of stearic acid formed by evaporation from benzene solution have shown that these crystals orient themselves upon any surface with the two shorter axes in the plane of the surface. These measurements show, furthermore, that the shorter axes are at right angles and have the lengths reported by Thibaud and Dupré la Tour. (We have not yet succeeded in determining a possible length and inclination for the *c* axis.) From these unpublished experiments we feel justified in believing that the very imperfect stearic acid crystals, with which we are concerned here, have the form of the α modification. We are unable to reconcile our angle 33° with the reported angle 39° 10′. It is, of course, possible that Thibaud and Dupré la Tour chose a unit cell in which the *c* axis is not parallel to the long hydrocarbon chain. No other choice would, however, have given an angle in agreement with ours without making the *c* axis too short to contain two molecules end-to-end, which is apparently the way they must be arranged.

We have given reasons above for believing that the pattern of Fig. 2*C* is formed by a single crystal, and we have calculated its orientation. We ought then to be able to account for the rather well defined spot pattern of this figure. In this we have not succeeded. Even if our data could be reconciled with those of Thibaud and Dupré la Tour, there would not be sufficient information at hand regarding relative intensities of different reflections from a crystal of the α modification. We are now engaged in studies of single crystals of this sort by the transmission method,[6] and hope soon to be able to clear up the present uncertainties.

It has seemed important to us to test whether or not the inclination of the hydrocarbon chains is the same in various stearic esters as in stearic acid itself. Microscopical examination of layers of methyl stearate deposited by evaporation from benzene solution has not disclosed any observable crystals. We conclude that they must be extremely small. This conclusion is in accord with the fact that diffraction patterns from different samples of methyl stearate are similar and indicate hydrocarbon chains randomly distributed in azimuth. Such a pattern is shown in Fig. 3. This yields $d=2.50$A and $\alpha=25°$.

The inclinations of the hydrocarbon chains of stearic acid (33°) and of methyl stearate (25°) differ by an amount which we believe greater than experimental error. This difference suggests that if we were to study higher single chain stearic esters we should find hydrocarbon chains standing more nearly normal to the supporting surface. We propose to carry out such investigations.

We are indebted to Dr. C. J. Davisson for many helpful suggestions and criticisms.

[3] Proc. Roy. Soc. **A114**, 542–561 (1927).
[4] Thibaud and Dupré la Tour, J. Chim. Phys. **29**, 153–167 (1932).
[5] See, however, Storks, Phys. Rev. **50**, 396 (1936).
[6] See Fig. 4 in a note by K. H. Storks and L. H. Germer, Phys. Rev. **50**, 676 (1936).

Linear or Edge Energy and Tension as Related to the Energy of Surface Formation and of Vaporization

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The free energy of the edge of a lens of a nonvolatile oil on water is found by a consideration of the magnitude of the molecular energy involved to be very small, and of the order of 3×10^{-6} erg per cm. Thus the linear tension of the edge should be of the order of 3×10^{-6} dyne. The smallness of the energy does not indicate a lack of importance of the edge, since the molecular energy is higher than in the surface. Linear energy and the presence of edges are of importance in practically all solids, since these are in general built up of crystal grains, and are of special significance in certain biological systems. Equations which give the relation between the free, latent and "total" energy of the edge and the latent heat of vaporization, are presented.

1. INTRODUCTION

WHERE two surfaces meet an edge is formed. This may be considered as a simple edge. A more complicated or multiple edge is produced by the meeting of a greater number of surfaces or interfaces and this is the only type which is stable for liquids. A surface may be considered to consist of a two-dimensional array of molecules: an edge by a linear array.

Where two or more edges meet, a point or angle is formed. Phases, surfaces, edges and points may all be indicated by the more general term *regions*. The energy of a certain amount of material increases in general as it is moved from a phase, or three-dimensional region, to a surface, and this increase continues when it is moved to an edge and then into a point. The increase of energy thus produced may be considered as potential energy insofar as there is equipartition of the kinetic energy.

The surface energy of any system is not the energy present in its surface regions, but only the excess of energy introduced by the presence of the surfaces. What may be termed the phasal energy is not considered as a part of the surface energy. Thus, if any surface region is considered to consist of a definite amount of material, the energy which this material would have in the phase is not included in the surface energy. The somewhat analogous, but more complicated relations of the linear energy are treated in Section 3.

The topics "linear wetting" and linear adsorption have been considered by Talmud and his associates[1] but they do not consider the magnitude of the linear energy, which is the subject of the present paper.

It is shown later in this paper that the magnitude of the edge energy is very small, but that this extreme smallness is not due to the smallness of the energy per molecule in the edge, but is due entirely to the extremely small number of molecules in one centimeter of an edge, as compared with the number in one square centimeter of surface or one cubic centimeter of a solid or liquid phase.

The extreme smallness of the linear or point energy does not mean that the presence of edges and of points is of necessity unimportant. It has been found, at least for nonpolar solids, that a point on a crystal has a higher solubility and a greater vapor pressure than an edge and that in an edge these are both larger than in a surface.

The fact that a given amount of material has a higher energy in a point or an edge is of particular importance in its effects upon the form of the minute subdivisions of biological systems, where the form of these subdivisions is of such great importance. Thus the importance of edges and of points may be said to be greatest in crystalline and especially in biological systems.

2. ORIENTATION OF MOLECULES IN EDGES

The theory of orientation of molecules in surfaces and interfaces may be applied, in the form

[1] D. L. Talmud, B. A. Talmud and S. E. Bresler, Physik. Zeits. Sowjetunion **4**, 854 (1933); S. E. Bresler, W. W. Druschinin and D. L. Talmud, Zeits. f. physik. Chemie **A164**, 389 (1933); D. L. Talmud, B. A. Talmud and S. E. Bresler, ibid. **A163**, 91 (1933).

in which it was developed by Hardy and Harkins,[2] to the orientation of the molecules in edges.

Thus, in a simple edge the least polar groups are oriented toward the sharpest part of the edge, in order to give the least possible value, under the conditions, to the free energy of the edge. The more exact relation is, obviously, that the free energy of the system is a minimum. In a multiple edge the orientation is such as to give all of the transitions at the edge as little abruptness as possible. That is the sum of all of the transitions from phase to edge, and from interface to edge is as small as possible in terms of the electrical fields involved. Thus active groups, such as NO_2, CN, COOH, COOM, COOR, NH_2, $NHCH_3$, NCS, COR, CHO, I, OH, or groups which contain N, S, O, I, or double bonds, turn toward the most polar phase, which is often water, or toward mercury, or toward a hydrophyllic solid, such as titanium dioxide, silicon dioxide, stannic oxide, oxides of the metals in general, barium sulphate, other salts, etc.

The hydrocarbon chain of an organic molecule in the edge in general orients itself preferably toward the vapor phase, or turns toward a nonpolar phase. Thus at an edge between octyl alcohol, water and vapor (with or without air) the abruptness of the transition between vapor and water, vapor and octyl alcohol, and octyl alcohol and water must all be as small, in terms of the molecular fields, as is possible. This means that the last row of octyl alcohol molecules exhibits an orientation with the nonpolar group toward the vapor, and the polar group between a polar hydroxyl group of the alcohol and a molecule of water.

3. Linear or Edge Energy and Tension

A unit area of the surface of a liquid or solid has a certain amount of free surface energy (γ) and also of what is commonly called total surface energy (h), in excess of that which would be present if there were no surface. It has been found that in ordinary pure liquids most of the surface energy is stored in the outermost layer one molecule thick, although some of it penetrates more deeply. In a liquid the free surface energy is made evident by a surface tension of the same magnitude. The relation between the free and the surface energy is given by the equation

$$\gamma+l=h,$$

in which l is the latent heat and h the Gibbs heat function or total surface energy. The entropy (s) of the surface is l/T which may be shown to be equal to $-(\partial\gamma/\partial T)_{A,\,P}$.

In this paper all terms in the equations are taken to represent one molecule. Thus in Eq. (1) γ represents the free surface energy for an area of surface occupied on the average by one molecule.

The internal latent heat of vaporization (λ) is given by Eq. (2)

$$\lambda=h+j=\gamma+l+j, \qquad (2)$$

in which (j) is the "jumping out energy" or energy of thermal emission from a surface.

An edge may be considered as a part of the surface or the interfacial region where one radius of curvature of at least one of the surfaces is extremely small. It is well known that the surface energy should increase as the surface curvature is increased (radius of curvature decreased) but even for ordinary small drops the increase in energy is negligible. This is, however, by no means the case as the drop approaches molecular dimensions.

For an edge the corresponding equations would by analogy be written as

$$\gamma_e+l_e=h_e \qquad (1')$$

and

$$\lambda=h_e+j_e=\gamma_e+l_e+j_e. \qquad (2')$$

These quantities do not have, as in Eqs. (1) and (2), entirely definite values, but may vary between maximum and minimum values, according to the conditions specified. Thus (1) since the magnitude of the surface energy terms is dependent upon the curvature, Eqs. (1) and (2) have constant valued terms only because they are defined as applicable to plane surfaces alone. An edge, however, must be considered as having different curvatures, according to its sharpness.

In addition (2) the values of the terms in the equations for linear energy are different depending upon whether they refer to the excess in energy over that in the phase or in the surface.

[2] W. B. Hardy, Proc. Roy. Soc. **A86**, 634 (1911–12); **88**, 303 (1913); W. D. Harkins, G. L. Brown, E. C. H. Davies, J. Am. Chem. Soc. **39**, 354 (1917).

Thus these equations become:

$$\gamma_{es}+l_{es}=h_{es}, \qquad (1^{II})$$

$$\lambda=h_{es}+j_{es}=\gamma_{es}+l_{es}+j_{es}, \qquad (2^{II})$$

referred to the surface, and when referred to a volume phase

$$\gamma_{ev}+l_{ev}=h_{ev}, \qquad (1^{III})$$

$$\lambda=h_{ev}+j_{ev}=\gamma_{ev}+l_{ev}+j_{ev}. \qquad (2^{III})$$

Eq. (2^{III}) may be used to obtain an idea of the order of magnitude of the linear energy and also of the linear tension. The value of λ is the same in Eq. (2) as in this equation. The effect of the edge is to increase the free surface energy γ and to decrease the energy of thermal emission, so

$$\gamma_e>\gamma, \qquad j_e<j. \qquad (3)$$

Also, it may be assumed that $l_e>l$.

4. Simple Edge of an Ideal Liquid Lens in Vapor or Air

Since the latent heat of vaporization (λ) is greater than the total edge energy (h_e) per molecule, the first step will be to obtain some idea of the order of magnitude of λ for the number of molecules assumed to be present in 1 cm of a simple liquid edge which represents a highly idolized system, since such a lens is not stable. Now

$$\lambda=sT,$$

where s is the entropy of vaporization per molecule. The Hildebrand-Trouton relation shows that for normal liquids the entropy is dependent upon the concentration of the vapor alone. Even with excessively dilute vapor the value is not over 20×10^{-16} erg per molecule per degree. Let it be supposed that the edge is so thin as to contain only a single row of molecules. Then the number of organic molecules in 1 cm of edge would commonly be 2.2×10^{7}.

On such a basis the value of λ at 300°K or ordinary temperature would be $300\times2.2\times10^{7}\times20\times10^{-16}$ erg or 1.3×10^{-5} erg. Since $\gamma=\lambda-l_e-j_e$, the value of the free linear energy and therefore of the linear tension should be less than 1.3×10^{-5} erg cm^{-1},

$$\gamma_{ev}<h_{ev}<\lambda=1.3\times10^{-5}\text{ erg cm}^{-1}.$$

In particular for ether the latent heat of vaporization per molecule is 9×10^{-6} erg for the number of molecules assumed to be present in the edge, while the free surface energy in a plane surface is 1.1×10^{-6} erg for this number of molecules, and the surface latent heat is 1.5×10^{-6} erg.

The value of the free linear energy γ_{ev} would then be equal to $1.1\times10^{-6}+\gamma_{es}$ erg. For a plane surface the energy of thermal emission (j) is 6.0×10^{-6} erg for this number of molecules, and the total surface energy is 3×10^{-6} erg.

A crude method of consideration may be adopted for an extremely sharp edge. The molecules may be considered as a linear array of cubes, with only a single linear array below them. Thus one-half of each cube would be exposed to the vapor, and the total linear energy (h_{ev}) may be taken as $\frac{1}{2}\lambda_i$ or $\frac{1}{2}\times9\times10^{-1}$ erg or 4.5×10^{-6} erg. If this is divided between latent heat and free energy in the same proportions as in a surface then the free linear energy γ_{ev} is about 2×10^{-6} erg per cm. These results are summarized in Table I.

From the values in Table I, since the linear tension is given by the linear free energy, the linear or edge tension for a sharp edge of ether should be of the order of 2×10^{-6} dyne.

The free linear energy and linear tension is calculated below by a different method. Consider the special case of water whose free surface energy is 72.75 ergs per sq. cm or 7.275×10^{-14} erg per molecule. Let the edge be one molecule thick and assume that three times as much of each molecule is exposed as in the surface. Then the free energy would be increased to 14.5×10^{-14} erg above what it is in the surface, or 21.7×10^{-14} erg above what it is in the interior of the liquid. Since there are 3.2×10^{7} molecules in 1 cm of the edge, the free linear energy is $\gamma_{es}=14.5$ or $\gamma_{ev}=21.7$

Table I. *Order of magnitude for the linear energy of a sharp edge of ethyl ether.*

	Ergs per cm $\times10^{6}$
Free linear energy referred to phase γ_{ev}	2
Free linear energy referred to surface	1
Total linear energy h_{ev}	4.5
Linear latent heat λ_{ev}	2.5

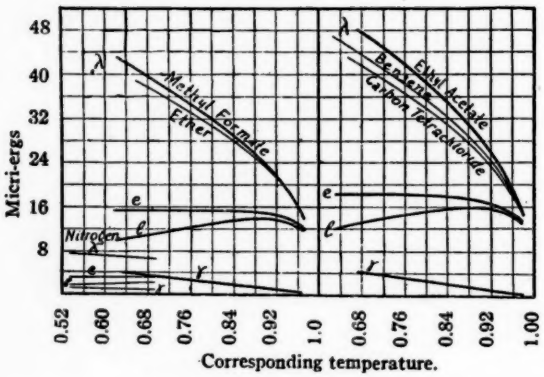

FIG. 1.

$\times 10^{-14}+3.2\times 10^{7}$, which gives $\gamma_{es}=4.6$ or $\gamma_{ev}=7\times 10^{-6}$ erg per cm or the linear tension is between 4.6 and 7×10^{-6} dyne.

At 20° the energy of vaporization of water for this number of molecules is 2.0×10^{-5} erg per cm, and for this number of molecules the edge energy must be less than the energy of vaporization.

5. Variation of Linear Energy with Temperature

The variation of the magnitude of the various terms in Eq. (1) which gives the latent heat of vaporization per molecule from a plane surface is represented for liquids by Figs. 1, 2, and 3. With the normal liquids the total surface energy is almost constant over the ordinary range of temperatures for which the liquids are used, but decreases extremely rapidly as the critical temperature is approached.

The free surface energy decreases rapidly and almost linearly with temperature, the latent heat of the surface rises rapidly and that of evaporation and of thermal emission falls rapidly with temperature.

It has been pointed out that curves which represent linear energies are not so definite. However, if the energy is referred to that of the interior of the phase as zero, then the curves have the same general form as in the figures. Evidently the curve for λ is unchanged, but that for γ_{ev} is raised ($\gamma_{ev}>\gamma$), so since this falls to zero at the critical temperature, its slope is greater. Since $l=-T(\partial\gamma/\partial T)$ this causes the latent heat to be higher ($l_{ev}>l$), and thus h_{ev} is higher than h ($h_{ev}>h$). This means that the energy of thermal emission is lower for the edge than for the surface ($j_{ev}<j$).

6. Effect of Thickness of the Edge

The preceding section indicates that the general order of magnitude of the linear tension for a sharp edge (angle acute) on a lens of an ordinary organic liquid in air is between 10^{-6} and 10^{-5} dyne. This is based upon the assumption that the edge energy is contained largely, not wholly, in a linear array one molecule in thickness. The early work of the writer and his collaborators[3] gives excellent evidence that most, though not all, of the surface energy of a liquid is contained in the first monomolecular layer, and it is well known that molecular forces from organic molecules lose almost their whole effect at greater than single molecular distances.

Suppose that the assumption is advanced that the edge is not monomolecular but highly polymolecular, say 100 molecules in thickness. Then the magnitude of the linear energy and linear tension is by no means multiplied by 100, since the total change of direction of the surface in the edge is dependent upon the angle in the edge alone. The thicker a surface the smaller its surface energy, since the transition from one phase to the other is thus made less abrupt.

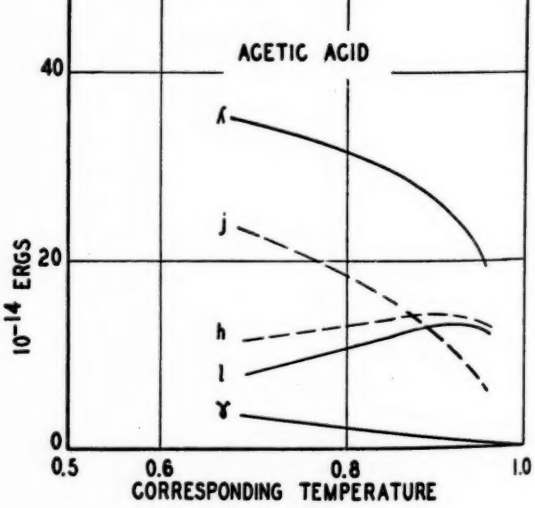

FIG. 2.

[3] Bibliography in Zeits. f. physik. Chemie **A139**, 689 (1929).

The existence of an edge tension for an organic liquid or water of 100 times the magnitude estimated above would be extremely difficult to explain on the basis of a thick edge, yet such a factor of multiplication would increase the estimate to only a value less than 0.001 dyne.

Thus, let it be supposed as above that an increase in thickness of the edge does increase the free energy of the edge. Then this increase by a factor of 100 must be caused by a very thick edge, since each molecular thickness cannot now give as much as 1/100 the effect in a monomolecular edge. On this basis the thickness of the edge corresponds to a distance of 10,000 molecules along the surface of 45 microns, which is entirely too great a distance to represent an edge at all. On this basis the linear tension should be much less rather than more than 0.001 dyne for organic liquids even if it is assumed that an edge is many molecules in thickness.

7. Edge or a Lens of Oil on Water

The calculations given above refer to a liquid lens in air, a case seldom or never realized. If a lens of oil rests upon the surface of water, then the magnitudes obtained above are not very greatly changed. Thus, while it may be considered that there are now two edges, one of oil and one of water, the energy of each edge is much lessened by the presence of the other. Also, if one edge is very sharp, the other will in general be much less sharp. The result of this is that there is a lowering of the linear energy and tension in somewhat the same way as the surface energy and tension of a liquid are lowered by the presence of a second condensed phase. Thus water has a surface tension of 72.75 dynes per cm at 20°, while that of benzene is 28.88. The interfacial tension between the two is 35.0 dynes, which is lower than the surface tension of the water, but higher than that of the oil. For a petrolatum the surface tension was found to be 30.8 and the interfacial tension 40.6. Similar values for many different organic liquids have been published.[4]

The surface tension of mercury at 20° is 476 dynes per cm and the interfacial tension is 375 toward water, 357 toward benzene, and 304 toward methyl iodide.[5]

When all of these magnitudes are considered it may be estimated that the linear tension of a lens of tetradecane on water would be about 3×10^{-6} dyne if the edge were sharp, or of the general order of 2×10^{-6} dyne for the actual edge, which is not sharp for the oil phase. It is obvious that the angle for the water part of the edge must be taken into consideration.

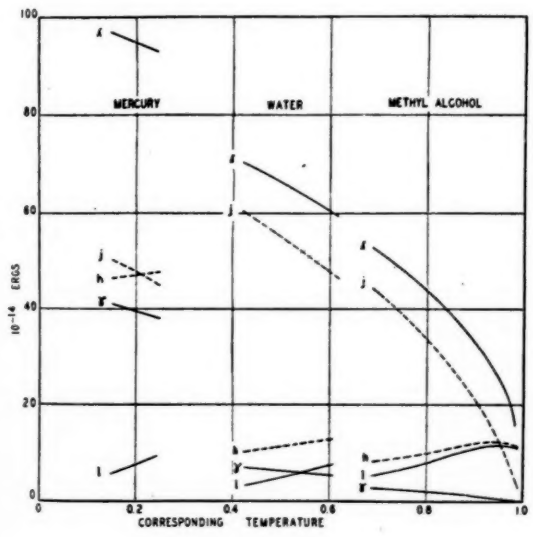

FIG. 3.

8. Edge of a Crystal

The magnitude of the linear or edge energy for an organic crystal may be expected to be of the same general order of magnitude as for the liquid. However, with inorganic crystals, especially, those of metals, the edge energy is undoubtedly very much higher. However, the surface energy of sodium chloride, while much higher than that of water, is not excessively high. Thus the magnitude of the linear energy of the edge of a cubic crystal of this salt is found by Lennard-Jones[6] to be 4.0×10^{-6} ergs per cm. The theory is more definite in this case, since the theory of the energy of an ionic lattice is well developed. The agreement in the order of magnitude between this and the value for a liquid edge as obtained from a

[4] W. D. Harkins, G. L. Clark and L. E. Roberts, J. Am. Chem. Soc. **42**, 700 (1920); W. D. Harkins and Y. C. Cheng, J. Am. Chem. Soc. **43**, 35 (1921).

[5] W. D. Harkins and E. H. Grafton, J. Am. Chem. Soc. **42**, 2534 (1920); W. D. Harkins and W. W. Ewing, J. Am. Chem. Soc. **42**, 2539 (1920).

[6] J. E. Lennard-Jones, Proc. Phys. Soc. **43**, 461 (1931).

consideration of molecular energy magnitudes, is as good as could be expected, since the value for the liquid edge should be several times lower, and it has been found to be about half as high.

Thus, according to both Lennard-Jones and the writer the linear tension should be of the general order or 2×10^{-6} dyne. The value of 6.54 dynes determined by Langmuir[7] is in violent disagreement with this. While the writer has not studied the mathematics used by Langmuir, it seems obvious that the magnitude which he obtains refers to something else than the true linear tension treated in the present paper.

[7] Langmuir, J. Chem. Phys. **1**, 762 (1933).

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Factors Influencing Rates of Reaction in Solution

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The factors which may influence the rates of reactions in solution have been classified and discussed with particular reference to the effect on A in the expression $Ae^{-E/RT}$ for the rate constant K. Means by which these different effects may be studied experimentally have been discussed. An explanation has been given of the tendency of A and E to change in the same direction, and of K and E to change in opposite directions, when comparison is made of the rate of a given unimolecular reaction in various solvents.

A NUMBER of recent communications[2] have dealt with the factors affecting reaction rates in solution. Since the ideas have not been developed very systematically, and since (insofar as we are aware) not all possibilities have been considered, we feel that it would be useful to present a classification and discussion of these factors.

It is customary in discussing a reaction rate constant to write it in the form $K=Ae^{-E/RT}$, where E, the activation energy, is the difference between the average energy of all *reacting* molecules, pairs or triplets and that of *all* molecules, pairs or triplets. A bears a somewhat similar relation to entropy differences, as has been fully discussed in recent publications. We shall refer to the *reacting* molecule, pair or triplet, as an activated complex, using the term in the generalized sense of Rice and Gershinowitz.[3] The term reactant or reactants will be used to denote the average state of the reacting system. We note the *general rule*, now well understood, that anything which places a restriction upon the activated complex decreases A, while anything which places a restriction upon the reactant increases A, since (excluding any indirect effect due to a concomitant change in the enery) it makes the configuration corresponding to the activated complex *relatively* more probable. A number of authors, in considering the effect of various factors on A and K, for reactions in solution, have introduced hypothetical intermediate steps, which involve the reacting substances or the activated complex in the gas phase or pure liquid phase. It is our opinion, however, that very little of the inherent complexity of the problem is avoided in this way and we prefer to restrict out considerations to the actual reacting systems, without introduction of hypothetical processes.

With this understanding, then, we may proceed with our classification. We may divide all the influences which affect reactions in solution into two classes, as follows:

I. Factors which also Obtain in Gas Phase

Under this heading we include such matters as the orientation or freezing out of rotations into vibrations in bimolecular associations. The effect

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[2] Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935); Evans and Polanyi, Trans. Faraday Soc. **31**, 875 (1935); Moelwyn-Hughes and Sherman, J. Chem. Soc. 101 (1936); Glasstone, ibid. 723 (1936).

[3] Rice and Gershinowitz, J. Chem. Phys. **3**, 482 (1935); Rice, ibid. **4**, 54 (1936).

of such factors on A has already been extensively discussed. They can also affect E, but this is of less interest. These factors operate in the same way in solution as in gas phase (or, at least, any difference is included in the discussion below) so that it is unnecessary to go further into the matter in this communication.

II. Factors which Obtain Only in Solution

These may again be divided into two classes:

1. The internal volume effects

A solute is not free to move through the whole volume of the solution,[4] since a large proportion of this volume is occupied by solvent molecules. Actually only a very small fraction of the volume is available. This fact can affect (a) the translational motion, (b) the rotational motion of solute molecules. In the case of a bimolecular reaction, or one of higher order, (a) must always operate to increase A, since the translational motion takes place in a smaller volume and the collision frequency is thus increased. The factor (b) may operate in either direction, depending upon whether the rotational motion of the activated complex or that of all the molecules is the more restricted. This in turn depends to a large extent on the number of rotational degrees of freedom involved in each case. The internal volume effect may also influence the energy of activation, for we can very well imagine a change of internal volume to take place on reaction. This will require work against or by the internal pressure, with corresponding effect on the energy of reaction and hence on the energy of activation of either the direct or the reverse reaction or both. We should, perhaps, add a few words about the possible magnitude of the internal volume effect. It certainly will not be as important as other effects, but estimates from entropies of vaporization indicate that in some cases the collision number in a bimolecular reaction can be increased by a factor of 20, considering the translational effect alone.[5] If the rotational entropy of the activated complex as compared to that of the reactant is also affected and in the same direction the increase in A may well be by a factor between 100 and 500.

2. Solvation effects

Solvation means less freedom for both solute and solvent molecule. That is to say (since the entropy is a measure of the freedom of motion of the molecules) if the reactant or the activated complex is solvated its entropy (in which we include also the entropy of the surrounding molecules of the liquid, which are really part of the reacting system) is lowered. Now a state which has a low entropy is an improbable state, so solvation will not occur unless the *energy* of the solvated state is less than that of the unsolvated state, and sufficiently less so that the probability of the solvated state is greater. The result of this situation, in the light of our general rule regarding the effect of the entropy and the probability of reactant and activated complex on the rate of reaction, is that solvation of the reactants increases A, increases E, and decreases K (since, by the general rule, the statement of the preceding sentence is equivalent to saying that the increase in E must be more than sufficient to counterbalance the increase in A), while solvation of the activated complex has just the opposite results.*

We believe that the above list of solution effects is, for all practical purposes, exhaustive, provided, at least, that we are dealing with a pure solvent and one which does not take part in the reaction.[6] Nevertheless, the factors are sufficiently varied and complicated, so that one may well wonder whether it will ever be possible to separate all of them experimentally. Bimolecular reactions involving complex organic substances, which have been so extensively studied in solution, are of the least favorable type from a theoretical point of view, since every one of the above factors is operative. It is therefore no wonder

[4] See Evans and Polanyi, Trans. Faraday Soc. **31**, 891 (1935).

[5] See, e.g., Rice, J. Chem. Phys. **4**, 371 (1936). Evans and Polanyi (reference 4) estimated a factor of 100.

* Since submission of this article for publication an article by Evans and Polanyi, Trans. Faraday Soc. **32**, 1333 (esp. p. 1358) (1936), containing some similar conclusions, has appeared.

[6] The above factors are all operative in the case of a mixed solvent, but certain complications can arise which we do not wish to consider in detail in this communication. We may, however, mention what some of these complications are. In a mixed solvent we may have solvation by any of the constituents of the solvent and compound formation between constituents of the solvent (including hydration of ions when the solvent is an electrolyte solution). It is, therefore, necessary to consider equilibria involving the various constituents of the solvent, as has been pointed out by Professor A. R. Olson in discussions with one of us.

that the values of A for such reactions vary over a wide range, and it would seem to be only a coincidence that the maximum number have a value of A corresponding to that expected for simple reactions in gas phase, neglecting internal volume effects.

It would appear that the only way to obtain independent information on the internal volume effect would be to study the bimolecular association of two atoms. In this case only translational motion would be involved, orientation effects of any kind would be eliminated, and with proper selection of reactant and solvent, solvation effects might be avoided. Iodine atoms would appear to offer nearly the only possibility, but even here the experimental difficulties would certainly be great.

It seems possible, however, to obtain information concerning solvation by comparison of the velocity constants for a given reaction in various pure solvents,[7] and also, when possible, by comparison of the reaction in solution with that in the gas phase. It seems plausible to assume that the internal volume effect will be similar for most solvents, and that the differences in reaction rate may be referred chiefly to differences in solvation. In fact, for the special case of unimolecular reactions which obey the hypothesis of exact orientation,[8] the internal volume effect will be negligible as far as A is concerned. For it is obvious that it can have no effect upon the translational part of the entropy of activation. If the hypothesis of exact orientation applies, the rotational degrees of freedom of the complex are identical with those of the reactant, and hence the internal volume can have no effect on the rotational part of the entropy of activation.

The unimolecular decomposition of N_2O_5 has been studied both in solution and in gas phase.[9] There is a number of solvents (so-called "normal" solvents) for which K, A and E are nearly identical with values for the gas phase reaction. In other solvents K is smaller, while A and E are larger than for the gas phase reaction.

The fact that a considerable number of liquids of various types act as normal solvents for this reaction suggests that the increase in activation energy due to the effect mentioned under II above is either negligible or is compensated by an increase of van der Waals forces accompanying the formation of the activated complex. Eyring and Daniels have suggested that the lower rate in abnormal solvents is due to the formation of a "complex" between the reactant and solvent molecules. The increase in E over that in normal solvents may reasonably be attributed to solvation energy of the reactant. By the above theoretical discussion (see II, 2) this should be accompanied by an increase in A and decrease in K, as is actually observed.

We may now extend the above reasoning to other examples of unimolecular reactions, assuming that the change in activation energy can be used as a measure of the amount of solvation. In the examples given by Moelwyn-Hughes[9] it is noted that A and E for a given reaction in various solvents generally increase or decrease together, and K varies in the opposite direction. That these relations should be true without exception is not to be expected, because the change in activation energy is by no means an exact measure of the change in the amount of solvation of the reactant or activated complex.[10]

In the case of nitrogen pentoxide it was possible to say that the reactant molecules were the solvated ones in abnormal solvents, because the rates were lower than the gas phase rates. Unless some standard is available, it will not be

[7] It should be pointed out that the effect of varying the composition of a mixed solvent is not necessarily similar to that of using different pure solvents, as will be clear from reference 6. The change of equilibria involving solvent molecules with the composition of the solvent may be such as to mask effects of the sort considered here. In addition, cases in which there is chemical reaction with the solvent, changing the nature of the reaction under consideration, must be excluded. Reaction with the solvent presumably occurs in the mutarotation of glucose, for example; thus the difference in A and E when the reaction takes place in H_2O or D_2O (Hamill and LaMer, J. Chem. Phys. **4**, 395 (1936)) is not covered in our discussion.

[8] Rice and Gershinowitz, reference 3, p. 481.

[9] Busse and Daniels, J. Am. Chem. Soc. **49**, 1257 (1927). Eyring and Daniels, ibid. **52**, 1473 (1930). For a discussion see Moelwyn-Hughes, *The Kinetics of Reactions in Solution* (Oxford, 1933), Chap. VI.

[10] The parallelism between E and A has been noted by a number of writers in the past (see, e.g., Roginsky and Rosenkewitsch, Zeits. f. physik. Chemie **B10**, 47 (1930); ibid. **B15**, 103 (1931); Syrkin, Zeits. f. anorg. Chemie **199**, 28 (1931)), but, as far as we are aware, the explanation offered in this paper has not been presented before. We feel that it is more reasonable than the explanation of Roginsky and Rosenkewitsch, which we believe to be scarcely consistent with the more recent theories of chemical reaction. Insofar as any parallelism between E and A for different reactions exists, it seems likely that the supposition of Pollisar (J. Am. Chem. Soc. **54**, 3105 (1932)), that it is merely accidental, is correct. Whether the relationships noted in the data we have been considering are to some extent accidental, also, is hard to decide, but the matter needs further experimental investigation.

possible to tell whether the reactant or the activated complex is solvated, but we feel that it is probable that it will usually be the reactant.

The method suggested for detecting solvation effects in unimolecular reactions, i.e., comparison of rates in various solvents, may also be extended to bimolecular reactions, and the same relations between E, A, and K, noted above, should obtain.[11] The available data[12] is not entirely conclusive. We may call attention to the addition reaction of ω-Br-acetophenone and aniline in various solvents. In this case it was found that the value of E is very low in benzene and chloroform as compared to various alcohols, acetone, and nitrobenzene. Corresponding to the low values of E are low values of A; but they are *too* low and, contrary to expectations, K is very much lower in benzene and chloroform than in the other solvents. However, this reaction undoubtedly involves a labile bromine, and hence specific reaction with the polar solvents (possibly ionization) cannot be excluded.

Another possibility for investigating solvation effects in bimolecular reactions appears to lie in the comparison of metatheses involving respectively an atomic and the corresponding ionic reactant.[13] As an example we may suggest the two optical inversions

$$I^-+RI\rightarrow IR+I^- \qquad \text{and} \qquad I+RI\rightarrow IR+I.$$

The first of these reactions should involve extensive solvation, while in most solvents the latter should not. It is to be expected that orientation and internal volume effects should be practically identical for the two reactions.

One of us (O. K. R.) wishes to acknowledge his indebtedness to the seminar of Professor A. R. Olson, which contributed greatly to the formation of his ideas concerning reactions in solution.

[11] However, since the internal volume effect is so much more important in bimolecular reactions, its difference in different solvents may need some consideration.

[12] For a summary see Holzschmidt, Zeits. f. anorg. Chemie **200**, 82 (1931).

[13] In this connection see the work by Young and Olson, J. Am. Chem. Soc. **58**, 1157 (1936), on some ionic reactions. Note especially p. 1162.

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Lattice Energies, Equilibrium Distances, Compressibilities and Characteristic Frequencies of Alkali Halide Crystals[1]

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Constants in the Born and Mayer exponential expression for the repulsion between two ions have been recalculated. Using these, the lattice energies and equilibrium distances between ions have been recomputed, for alkali halide crystals. Expressions have been derived and tested for the calculation of the compressibility and the characteristic maximum infrared frequency. The relation between these two quantities is shown to be approximated by an empirical equation proposed by Madelung.

RECALCULATION OF "a," LATTICE ENERGIES AND BASIC RADII

THE average potential energy per "molecule" in a crystal composed of univalent ions symmetrically surrounded, as in structures of the NaCl and CsCl types, can be expressed[3, 4] by the equation

$$\Phi=-\frac{\alpha e^2}{r_0}-\frac{C}{r_0^6}-\frac{D}{r_0^8}+bc_{+-}Me^{a(r_++r_--r_0)}+\frac{bc_{--}M'}{2}e^{a(2r_--k_2r_0)}+\frac{bc_{++}M'}{2}e^{a(2r_+-k_2r_0)}, \tag{1}$$

where r_0 = the distance between closest ion centers, obtainable from x-ray data[5] or from the

[1] This paper was presented at the Pittsburgh Meeting of the American Chemical Society, September, 1936.

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[3] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

[4] M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

[5] P. P. Ewald and C. Hermann, *Strukturbericht 1913–1928* (Akad. Verlagsgesellschaft, Leipzig, 1931).

density;

e = the electron charge (4.77×10^{-10} e.s.u.) in the first term and the basis of natural logarithms elsewhere;

C and D = van der Waals attraction constants;[6, 7]

b = an arbitrary constant, taken for convenience as 10^{-12} erg;

c_{+-}, c_{--} and c_{++} = factors introduced[8] to allow (roughly) for the dependence of the repulsion between two ions on their charges;

α = Madelung's constant;

M and M' = the number of nearest unlike and like neighbors, respectively;

k_2 = the ratio of the shortest distance between like neighbors to that (r_0) between unlike neighbors;

r_+ and r_- = "basic radii" of the positive and negative ions, respectively; $(r_+ + r_-)$ is the equilibrium distance for two ions of opposite sign when the total attraction energy has the value $-bc_{+-}$;

a is a quantity assumed to be constant (i.e., independent of r) for a given crystal.

Born and Mayer[3] computed a for the alkali halides from compressibility and thermal expansion data, finding it to be roughly the same for all, the average value being about 2.90 (Table III, col. 13).[9]

TABLE I.

1	2 LiX	3 NaX, KX, RbX, CsF	4 CsCl, CsBr, CsI
α	1.7476	1.7476	1.7626
c_{+-}	1.375	1.000	1.000
c_{++}	2.00	1.25	1.25
c_{--}	0.75	0.75	0.75
M	6	6	8
M'	8	8	6
k_2	1.414	1.414	1.155
k_1	2.000	2.000	1.540

[6] F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).
[7] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933).
[8] L. Pauling, Zeits. f. Krist. **67**, 377 (1928).
[9] a is the reciprocal of the ρ used in references 3 and 4. The change from ρ to a in this paper is made to conform with the usual practice in equations for the energy of a diatomic molecule.[10, 11] Throughout this paper, a is given in units of 10^8 cm^{-1}.

The lattice energy of an alkali halide crystal at the absolute zero is obtained by adding to the potential energy given by Eq. (1) a term $\epsilon = -\frac{9}{4}\nu_{max}$ for the average oscillational energy and summing over all the ions.

Using $a = 2.90$, Mayer and Helmholz[12] calculated lattice energies for these compounds (Table III, col. 16) and Huggins and Mayer[4] computed a set of basic radii (Table II, col. 2) from which the interionic equilibrium distances could be accurately calculated (Table III, col. 11).

Wishing to use Eq. (1) and expressions derived therefrom in some further work, the writer has recalculated a and the lattice energies. This seemed advisable for the following reasons:

1. In their calculations for the lithium halides, Born and Mayer and Mayer and Helmholz used incorrect values of the coefficients c_{+-} and c_{++}.[13]

2. For r_+ and r_- they used the Goldschmidt ionic radii, which are a poor approximation to the true basic radii.

3. More accurate values of compressibilities, coefficients of thermal expansion, van der Waals attraction constants and other quantities entering into the calculations are available than those used before.

4. Most of the data used in the calculation of a are for a temperature of 298°K or thereabouts, rather than 273°K, the temperature used by Born and Mayer. (The difference in results due

TABLE II. *Basic radii.*

1	2 $a = 2.90$	3 $a = 3.00$
	10^{-8} cm	10^{-8} cm
Li^+	0.475	0.570
Na^+	0.875	0.940
K^+	1.185	1.235
Rb^+	1.320	1.370
Cs^+	1.455	1.510
F^-	1.110	1.050
Cl^-	1.475	1.435
Br^-	1.600	1.560
I^-	1.785	1.750

[10] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[11] M. L. Huggins, J. Chem. Phys. **3**, 473 (1935); **4**, 308 (1936).
[12] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932).
[13] M. Born and M. Göppert-Mayer, "Dynamische Gittertheorie der Kristalle," *Handbuch der Physik*, Vol. 24, 2nd part, second edition (1933), p. 722.

to this temperature difference is very small, however.)

The constants and experimental quantities used in the first recalculation of a are collected in Table I, column 2 of Table II, and columns 3, 5, 6 to 8, and 17 of Table III. The average a obtained was about 3.0, instead of the previous 2.9. Using this new value, the basic radii were then recalculated, the new results being given in column 3 of Table II. With these, a was once more computed for each compound, the results (Table III, column 14) differing only slightly from those obtained with the older radii.

The lattice energies computed, taking $a=3.00$ and using the corresponding basic radii, are compared with those of Mayer and Helmholz and with experimental values in columns 15 to 17 of Table III.

Interionic equilibrium distances, computed with the new a and basic radii, are compared with the experimental distances and with those computed by Huggins and Mayer in columns 10 to 12 of Table III. The average deviation between the experimental values and those newly calculated is now only 0.006A

Calculation of Compressibilities

Born and Mayer's[3] Eq. (11) can be rewritten as

$$\beta=\frac{9k_1r_0^3F_{T,P}}{r_0^2(d^2\Phi/dr^2)} \tag{2a}$$

with

$$F_{T,P}=1+\frac{T}{\beta}\left(\frac{\partial\beta}{\partial T}\right)_P+\frac{T}{\beta^2V}\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial\beta}{\partial P}\right)_T+\frac{2T}{3V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{2b}$$

k_1 is the molecular volume (V/N) divided by r_0^3. (See Table I.) The denominator of Eq. (2a) is given by the expression

$$r_0^2\frac{d^2\Phi}{dr^2}=(bc_{+-}Ma^2)r_0^2e^{a(r_++r_--r_0)} \tag{3a}$$
$$\times[1+S(1+k_2)e^{(1-k_2)ar_0}]-\left[\frac{2\alpha\epsilon^2}{r_0}+\frac{42C}{r_0^6}+\frac{72D}{r_0^8}\right]$$

with

$$S=\left(\frac{c_{--}}{c_{+-}}\right)\left(\frac{M'}{2M}\right)a\left[1+\left(\frac{c_{++}}{c_{--}}\right)e^{2a(r_+-r_-)}\right]e^{a(r_--r_+)}. \tag{3b}$$

Calculation of $F_{T,P}$ from the experimental quantities listed in columns 6, 7, 8 and 19 of Table III show it (column 18) to have a value within a few hundredths of 1.00 in nearly all of the compounds with which we are concerned. Hence we may write as an approximation

$$\beta\approx\frac{9k_1r_0^3}{r_0^2(d^2\Phi/dr^2)}. \tag{4}$$

Although the two quantities enclosed in square brackets in Eq. (3a) are by no means negligible, the error caused by the neglect of one is to a considerable extent offset by that introduced by the neglect of the other. Hence, as a further approximation, one can use the relatively simple equation

$$\beta\approx\frac{9k_1r_0}{M}[bc_{+-}a^2e^{a(r_++r_--r_0)}]^{-1}. \tag{5}$$

The values of β calculation from Eqs. (2), (4) and (5) (using $a=3.00$ and the corresponding radii) are given in columns 20, 21 and 22 of Table III for comparison with the experimental results of column 19. The calculated values are on the whole low, yet the agreement (between columns 19 and 20) is not bad except in those cases (LiCl, LiBr, LiI, NaI, CsCl, CsBr, CsI) for which the repulsion between *like* ions is important. Perhaps Born and Mayer's assumption that the same value of a can be used for the more distant (like) atoms as for the closest (unlike) atoms is not a sufficiently good approximation, or the c_{+-}, c_{++} and c_{--} factors introduced by Pauling may be too far off. (Certain theoretical considerations lead the writer to believe that these factors, when not equal to unity, should be considerably closer to it than assumed by Pauling.)

Calculation of the Characteristic Maximum Frequencies

The characteristic maximum infrared frequency ν_{max} is customarily assumed, for an alkali halide crystal, to be the frequency of oscillation of the lattice of alkali ions, moving

TABLE III.

	2	3	4	5	6	7	8	9
	van der Waals Constants (Ref. 7)				$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$	$-\frac{1}{\beta}\left(\frac{\partial \beta}{\partial P}\right)_T$	ϵ
Formula	c 10^{-60} erg cm^6	C 10^{-60} erg cm^6	d 10^{-76} erg cm^8	D 10^{-76} erg cm^8	10^{-5} deg^{-1}	10^{-4} deg^{-1}	(Ref. 16) 10^{-12} barye^{-1}	10^{-12} erg
LiF	0.8	18	0.6	11	9.2[15]	2[18]	15.3	0.14
LiCl	2.0	113	2.4	104	12.2[15]	7[18]	19.8	(.10)
LiBr	2.5	183	3.3	190	14.0[15]	8[18]	24.3	(.10)
LiI	3.3	363	5.3	470	16.7[15]	(8)	37.3	(.08)
NaF	4.5	46	3.8	31	9.8[15]	(2)	17.5	.11
NaCl	11.2	180	13.9	180	11.0[15]	7[18]	24.6	.07
NaBr	14.0	271	19.0	300	11.9[15]	8[18]	25.5	.06
NaI	19.1	482	31.0	630	13.5[15]	(8)	40.0	.05
KF	19.5	167	21.0	150	10.0[15]	1[18]	20.2	(.08)
KCl	48.0	452	73.0	560	10.1[15]	5[18]	27.2	.06
KBr	60.0	605	99.0	800	11.0[15]	6[18]	31.9	.05
KI	82.0	924	156.0	1420	12.5[15]	6[18]	36.7	.04
RbF	31.0	278	40.0	290	(9.5)	(5)	(21.0)	(.07)
RbCl	79.0	691	134.0	960	9.85[15]	7.8[16]	(30.0)	.05
RbBr	99.0	898	180.0	1340	10.4[15]	(8)	35.0	.04
RbI	135.0	1330	280.0	2240	11.9[15]	(8)	43.0	.03
CsF	52.0	495	78.0	600	9.5[15]	10.2[16]	28.4	(.07)
CsCl	129.0	1530	250.0	2600	13.65[17]	8.8[16]	34.0	.04
CsBr	163.0	2070	340.0	3600	13.9[17]	9.1[16]	42.7	.03
CsI	224.0	2970	520.0	5800	14.6[17]	6.8[16]	49.0	(.03)

	10	11	12	13	14	15	16	17
	r_0			$a=\frac{1}{\rho}$		Lattice Energy per Mole		
Formula	exp. (Ref. 5) 10^{-8} cm	H & M (Ref. 4) 10^{-8} cm	H 10^{-8} cm	B & M (Ref. 3) 10^8 cm^{-1}	H 10^8 cm^{-1}	exp. kcal.	M & H (Ref. 12) kcal.	H kcal.
LiF	2.010	2.002	2.002	2.80	3.17		240.1	243.6
LiCl	2.572	2.557	2.564	2.62	2.87		199.2	200.2
LiBr	2.745	2.748	2.741	2.62	2.74		188.3	189.5
LiI	3.000	3.020	3.013	2.17	2.41		174.1	176.1
NaF	2.310	2.318	2.314		3.09		213.4	215.4
NaCl	2.814	2.810	2.817	3.07	3.17	181.3[20]	183.1	183.5
NaBr	2.981	2.981	2.981	2.99	3.15		174.6	175.5
NaI	3.231	3.229	3.230	2.60	2.74		163.9	164.3
KF	2.665	2.685	2.673	3.14	2.98		189.7	192.5
KCl	3.139	3.127	3.131	3.16	3.14		165.4	167.9
KBr	3.293	3.286	3.287	3.07	3.09		159.3	161.3
KI	3.526	3.521	3.525	2.85	2.93	153.8[21]	150.8	152.4
RbF	2.815	2.845	2.837		3.09		181.6	183.0
RbCl	3.270	3.267	3.273	2.81	3.15		160.7	162.0
RbBr	3.427	3.422	3.427	2.94	3.03	151.3[20]	153.5	156.1
RbI	3.663	3.653	3.663	2.85	3.01		145.3	148.0
CsF	3.004	2.996	3.004		3.68		173.7	175.7
CsCl	3.566[19]	3.572	3.580	3.23	3.11		152.2	153.1
CsBr	3.713	3.709	3.712	3.06	2.94		146.3	149.6
CsI	3.95	3.931	3.936	2.82	2.76	141.5[21]	139.1	142.5

as a unit, relative to the lattice of halide ions. Assuming this, we can calculate this frequency from the relation

$$\nu_{\max}=(k/4\pi^2\mu)^{\frac{1}{2}}, \tag{6a}$$

where μ is related to the masses of the individual ions by the equation

$$\mu=m_+m_-/m_++m_- \tag{6b}$$

and k is the coefficient of Δ (the displacement of one lattice relative to the other) in the expansion of $d\Phi/d\Delta$ as a power series in Δ.

For a crystal of the NaCl type, with the oscillations of the two lattices in one of the directions of the center lines between closest atoms, we can write (neglecting terms which do not vary with Δ and considering only the 6 closest ions)

$$\Phi=-e^2\left[\frac{1}{r_0-\Delta}+\frac{1}{r_0+\Delta}+\frac{4}{(r_0^2+\Delta^2)^{\frac{1}{2}}}\right]$$
$$-c\left[\frac{1}{(r_0-\Delta)^6}+\frac{1}{(r_0+\Delta)^6}+\frac{4}{(r_0^2+\Delta^2)^3}\right]$$
$$-d\left[\frac{1}{(r_0-\Delta)^8}+\frac{1}{(r_0+\Delta)^8}+\frac{4}{(r_0^2+\Delta^2)^4}\right]$$
$$+bc_{+-}[e^{a(r_++r_--r_0+\Delta)}+e^{a(r_++r_--r_0-\Delta)}$$
$$+4e^{a[r_++r_--(r_0^2+\Delta^2)^{\frac{1}{2}}]}]. \tag{7}$$

(In this equation, c and d are the van der Waals attraction constants for a single pair of unlike ions.) On differentiating, expanding in powers of Δ, and collecting terms, one obtains

$$d\Phi/d\Delta=[2bc_{+-}a^2(1-2a^{-1}r_0^{-1})e^{a(r_++r_--r_0)}$$
$$-60cr_0^{-8}-112dr_0^{-10}]\Delta$$
$$+\text{terms in higher powers of }\Delta. \tag{8}$$

TABLE III.—(*Continued.*)

	18	19	20	21	22	23	24	25	26
	$F_{T,P}$	β				$\nu_{\max}$			C'
Formula	(Eq. 2b)	exp. (Ref. 16) 10^{-12} barye^{-1}	(Eq. 2) 10^{-12} barye^{-1}	(Eq. 4) 10^{-12} barye^{-1}	(Eq. 5) 10^{-12} barye^{-1}	exp. (Ref. 22) 10^{12} sec^{-1}	(Eq. 9) 10^{12} sec^{-1}	(Eq. 11) 10^{12} sec^{-1}	(Eq. 17) 10^{8} cm sec^{-1}
LiF	0.72	1.17	0.88	1.22	1.56	9.21	12.18	14.42	1.25
LiCl	1.02	3.41	2.36	2.31	3.41		9.37	9.48	1.18
LiBr	1.03	4.31	2.64	2.57	4.20		8.94	8.33	1.17
LiI	0.96	6.01	2.75	2.86	5.58		7.57	7.37	1.16
NaF	0.84	2.11	1.82	2.17	2.01	7.40	8.13	8.30	1.21
NaCl	1.06	4.263	3.95	3.72	3.58	4.91	6.17	5.76	1.17
NaBr	1.08	5.08	4.43	4.09	4.12	4.02	5.20	4.85	1.16
NaI	1.04	7.07	5.06	4.87	5.45	3.51	4.61	4.14	1.15
KF	0.87	3.30	2.69	3.10	2.77		6.70	6.61	1.18
KCl	1.03	5.63	5.67	5.53	4.25	4.25	5.06	4.66	1.15
KBr	1.05	6.70	6.58	6.29	4.89	3.40	4.12	3.71	1.14
KI	1.04	8.54	7.65	7.32	5.94	2.94	3.67	3.21	1.13
RbF	1.02	4.1	3.32	3.25	3.06		5.96	5.57	1.17
RbCl	1.12	6.65	6.55	5.85	4.38	3.54	4.35	3.79	1.14
RbBr	1.12	7.94	7.64	6.81	5.05	2.63	3.27	2.79	1.14
RbI	1.10	9.57	9.13	8.27	6.21	2.32	2.78	2.36	1.13
CsF	1.13	4.25	4.50	3.97	3.78		5.34	5.51	1.16
CsCl	1.06	5.95	4.80	4.54	4.39	2.94	3.11	3.03	1.43
CsBr	1.05	7.06	5.72	5.46	4.90	2.24	2.27	2.14	1.42
CsI	0.98	8.57	6.55	6.67	6.00		1.89	1.77	1.41

Note: Values in parenthesis are estimated.

[15] F. A. Henglein, Zeits. f. Elektrochem. **31**, 424 (1925).
[16] P. Bridgman, Proc. Am. Acad. **67**, 345 (1932).
[17] G. P. Baxter and C. F. Hawkins, J. Am. Chem. Soc. **38**, 266 (1916).
[18] *International Critical Tables.*
[19] E. Brook, I. Oftedahl and A. Pabst, Zeits. f. physik. Chemie **B3**, 209 (1929).
[20] L. Helmholz and J. E. Mayer, J. Chem. Phys. **2**, 245 (1934).
[21] J. E. Mayer, Zeits. f. Physik. **61**, 798 (1930). See also reference 11.
[22] R. B. Barnes, Zeits. f. Physik **75**, 723 (1932).

(The Coulomb terms exactly cancel out.)

Precisely the same equation is obtained for oscillation of the two lattices in other directions relative to each other, e.g., in the directions of a face diagonal or a body diagonal of the unit cube.

Substituting the coefficient of Δ in Eq. (8) for k in Eq. (6a),

$$\nu_{\max}=(2\pi^2\mu)^{-\frac{1}{2}}[bc_{+-}a^2(1-2a^{-1}r_0^{-1}) \times e^{a(r_++r_--r_0)}-30cr_0^{-8}-56dr_0^{-10}]^{\frac{1}{2}}. \quad (9a)$$

Correspondingly, for a CsCl type crystal,

$$\nu_{\max}=(2\pi^2\mu)^{-\frac{1}{2}}[bc_{+-}a^2(1-2a^{-1}r_0^{-1})e^{a(r_++r_--r_0)} -40cr_0^{-8}-(224/3)dr_0^{-10}]^{\frac{1}{2}}. \quad (9b)$$

The frequencies calculated by means of these equations are compared with the experimental frequencies obtained by Barnes[22] in Table III, columns 23 and 24. The calculated results average about 20 percent higher than the experimental.

The van der Waals terms in Eqs. (9a) and (9b) are relatively small (in most cases less than 10 percent of the quantity from which they are subtracted), hence

$$\nu_{\max}=\left[\frac{(1-2a^{-1}r_0^{-1})}{2\pi^2\mu}(bc_{+-}a^2e^{a(r_++r_--r_0)})\right]^{\frac{1}{2}}. \quad (10)$$

Combining this with Eq. (5) for the compressibility gives the simple relation

$$\nu_{\max}\approx\left[\left(\frac{9k_1(1-2a^{-1}r_0^{-1})}{2\pi^2M}\right)\frac{r_0}{\mu\beta}\right]^{\frac{1}{2}}. \quad (11)$$

This has been used to compute the frequency values of column 25, Table III. The calculated quantities are about 9 percent higher than the experimental, on the average.

Madelung[14] has proposed, from dimensional considerations, the following relationship:

$$\lambda_{\min}=C'\left[\frac{(M_+M_-)^{\frac{3}{2}}}{(M_++M_-)^2}\right]^{\frac{1}{3}}\rho^{1/6}\beta^{1/2}. \quad (12)$$

Here $\lambda_{\min}$ is the wave-length corresponding to the maximum frequency $\nu_{\max}$, M_+ and M_- are the ordinary atomic weights, ρ is the density, and C' is a constant determined empirically. If we substitute

$$\lambda_{\min}=c_0/\nu_{\max}, \quad (13)$$

c_0 being the velocity of light,

$$\rho=m_++m_-/k_1r_0^3, \quad (14)$$

$$M_+=Nm_+, \quad (15a)$$

and

$$M_-=Nm_-, \quad (15b)$$

N being Avogadro's number, we obtain

$$\nu_{\max}=\left[\left(\frac{c_0^2k_1^{\frac{1}{3}}}{C'^2N^{\frac{1}{3}}}\right)\frac{r_0}{\mu\beta}\right]^{\frac{1}{2}}. \quad (16)$$

This is obviously of the same form as Eq. (11), C' being given by

$$C'\approx\left(\frac{2^{\frac{1}{2}}\pi c_0}{3N^{\frac{1}{3}}}\right)\left(\frac{M^{\frac{1}{2}}}{k_1^{\frac{1}{2}}}\right)(1-2a^{-1}r_0^{-1})^{-\frac{1}{2}}. \quad (17)$$

Although not strictly the same for different alkali halide crystals, C' does not vary greatly for those of the same structure type, as may be seen from column 26 of Table III.

Conclusion

The results of the lattice energy and interionic distance calculations, using Eq. (1) with the new values of a, r_+ and r_-, are believed to be even better than those computed earlier. Taking the interactions between ions to be as assumed in the derivation of that equation, it has been shown that the compressibility and the characteristic maximum infrared frequency can be calculated with reasonable accuracy. An approximate equation relating the compressibility and this maximum frequency has been derived, tested, and shown to agree roughly with Madelung's empirical relationship.

[14] E. Madelung, *Göttingen Nachr.* (1909), 100; (1910), 43; Physik. Zeits. **11**, 898 (1910); M. Born and M. Göppert-Mayer, reference 13, p. 656.

A Test of the Third Law of Thermodynamics by Means of Two Crystalline Forms of Phosphine. The Heat Capacity, Heat of Vaporization and Vapor Pressure of Phosphine. Entropy of the Gas

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The heat capacity of solid and liquid phosphine has been measured from 15°K to its boiling point, 185.38°K. Transitions were found at 30.29, 49.43 and 88.10°K. The heats of transition are 19.6, 185.7 and 115.8 cal./mole, respectively. The transition at 49.43°K had not previously been reported. In order to obtain complete conversion to the form of phosphine which is stable below 49.43°K it was necessary to keep the unstable form near 40°K for several days. A graph showing the rate of conversion to the stable form as a function of temperature has been given. The transition at 30.29°K occurs in the form of phosphine, unstable below 49.43°K. There is also a region of abnormally high heat capacity in the supercooled form between 30.29 and 35.66°K. At the latter temperature the heat capacity decreases abruptly by 15 percent without evidence of latent heat. The melting point was found to be 139.35°K and the heat of fusion 270.4 cal./mole. The heat of vaporization at the boiling point, 185.38°K, was determined calorimetrically. The value found was 3489 cal./mole. The vapor pressure of solid and liquid phosphine was measured and the results represented by the equations: Solid phosphine 128.67 to 139.35°K; $\log_{10} P$(int. cm Hg) $= -895.700/T + 6.86434$. Liquid phosphine 139.35 to 185.56°K; $\log_{10} P$(int. cm Hg) $= -1027.300/T - 0.0178530T + 0.000029135T^2 + 9.73075$. The entropy of the solid at 49.43°K may be obtained either from measurement on the stable or unstable form. The values are 8.14 and 8.13 cal./deg. per mole, respectively. While the extraordinarily close agreement is somewhat fortuitous, the measurements provide the most accurate existing verification of the third law of thermodynamics by means of two crystalline forms of a substance. The molal entropy of the ideal phosphine gas at the boiling point was found to be 46.39 ± 0.1 cal./deg. per mole. The corresponding value at 298.1°K is 50.35 cal./deg. per mole. This may be compared with the value 50.5 calculated by Yost with the assistance of spectroscopic data and an estimated bond angle. The above entropy values neglect the nuclear spin entropy, $R \ln 16 = 5.509$ cal./deg. per mole, which should be added to obtain the absolute entropy. The values given are the ones which should be used in ordinary thermodynamic calculations. Phosphine is known to be a symmetrical top and the two equal moments of inertia are known from its band spectrum. It has not been found possible to evaluate the other moment of inertia in this manner. However, it can be calculated from the accurate entropy determination given above. The value found is $I_C = (7.9 \pm 0.8) \times 10^{-40}$ gram cm^2. The $P-H$ distance was found to be 1.45 ± 0.02A and the bond angle, $98 \pm 5°$.

IN this paper we will present the results of a low temperature investigation of phosphine. During this research a new form of phosphine, stable below 49.43°K, was discovered. By means of the new modification and the previously known form, which has now been shown to be unstable at low temperatures, it has been possible to obtain what we believe to be the most accurate verification of the third law of thermodynamics, using two crystalline forms of a substance.

The entropy of the gas has been evaluated from the calorimetric measurements. The entropy may also be obtained with the assistance of spectroscopic data. While the interpretation of the band spectrum of phosphine is not as complete as might be desired, nevertheless it has been possible to prove that the third law value of the entropy is in agreement with that given for the gas by quantum statistics.

[1] Charles A. Coffin Fellow, academic year 1934–35.

APPARATUS

The apparatus and methods employed in this research are similar to those used in previous investigations on condensed gases in this laboratory. The calorimeter is the one which has been given the laboratory designation Gold Calorimeter II.[2,3] A full description of a similar calorimeter has been given by Giauque and Egan.[4] The temperatures were measured and heat introduced by means of a gold resistance thermometer heater. The resistance thermometer was calibrated during the measurements against copper constantan thermocouple W, which was soldered to the bottom of the calorimeter. This thermocouple had been compared with a hydrogen gas thermometer,[5] and oxygen and

[2] Giauque and Wiebe, J. Am. Chem. Soc. **50**, 101 (1928).
[3] Blue and Giauque, ibid. **57**, 991 (1935).
[4] Giauque and Egan, J. Chem. Phys. **5**, 45 (1937).
[5] Giauque, Buffington and Schulze, J. Am. Chem. Soc. **49**, 2343 (1927).

hydrogen vapor pressure thermometers,[6] by former investigators in this laboratory. At the conclusion of this research, the thermocouple was again checked against the triple point of hydrogen, hydrogen vapor pressures, the 43.76°K transition temperature of oxygen, and the triple point and vapor pressures of oxygen. The thermocouple gave temperatures which were low by the following amounts: 0.17° at the triple point of hydrogen, 13.95°K; 0.15° at the boiling point of hydrogen, 20.37°K; 0.13° at the transition temperature of oxygen, 43.76°K; 0.11° at the triple point of oxygen, 54.39°K; 0.01° at the boiling point of oxygen, 90.13°K. Suitable corrections were applied to the original calibration.

As is well known, small changes in physical state, which may produce a negligible effect on the electrical properties of metals at ordinary temperatures, commonly produce rather large effects at very low temperatures. The small low temperature deviations from the original calibration which was made nine years before these measurements demonstrate that very reliable copper constantan thermocouples can be made. It may be recalled, however, that Giauque, Buffington and Schulze[5] tested 58 spools of constantan wire at low temperatures, before selecting the particular wire from which this thermocouple was made.

It was considered unnecessary to reinvestigate the thermocouple above 90°K since not only was it in agreement at this temperature but the rapidly increasing dE/dT makes small changes in e.m.f. relatively less important at higher temperatures.

Preparation and Purity of Phosphine

Phosphine was prepared by the action of potassium hydroxide on phosphonium iodide. The phosphonium iodide was made from white phosphorus, iodine and water by the method of Baeyer.[7] The reaction is represented by the equation

$$9P+5I+16H_2O=5PH_4I+4H_3PO_4.$$

The yellowish brown product was sublimed into the generating flask to give clear colorless crystals.

To the phosphonium iodide, a twenty-five percent solution of potassium hydroxide was added slowly. The evolved phosphine was washed by hydrochloric acid to remove any P_2H_4, and then by a solution of potassium hydroxide to remove hydrochloric and hydroiodic acids. Finally, the gas was dried by KOH sticks and phosphorus pentoxide, and condensed in a liquid-air trap protected by a thin metal jacket. About 250 cc of liquid phosphine were prepared in this manner, and over half of this was discarded in the fore and end portions of several distillations. The solid phosphine was subjected to a high vacuum before the product was distilled into the calorimeter.

A series of short heat capacity measurements were made in the temperature region immediately below the melting point in order to determine the premelting effect due to liquid-soluble solid-insoluble impurity. From these measurements it was calculated that the impurity was less than four moles in one hundred thousand moles.

The gas prepared in the above manner was always spontaneously inflammable, although the moist gas, as it first came from the phosphonium iodide, was usually not. When the dry gas was moistened by bubbling through a trap containing water, it no longer ignited on contact with air. Since the dry gas was later shown to be very pure, it may be concluded that the pure gas is spontaneously inflammable. This confirms the similar observation of Ritchie.[8]

Vapor Pressure of Phosphine

The vapor pressure of phosphine was measured by means of a manometer 1.6 cm in diameter. The measurements were made by using a cathetometer as a comparison instrument in connection with a standard meter mounted in the manometer case. The pressure observations are corrected to international centimeters of mercury by means of data given in the *International Critical Tables*.[9] The standard accelera-

[6] Giauque, Johnston and Kelley, J. Am. Chem. Soc. **49**, 2367 (1927).
[7] Baeyer, Annalen **155**, 266 (1870).
[8] Ritchie, Proc. Roy. Soc. London **A128**, 551 (1930).
[9] *International Critical Tables* (McGraw-Hill Book Co., New York, 1926).

TABLE I. *Vapor pressure of phosphine.* (*Boiling Point 185.38°K, 0°C=273.10°K.*)

T°K	P(int. cm Hg) (OBSERVED)	P OBS. −P CALC.	T OBS. −T CALC.
128.67	0.798	−0.002	+0.01 Solid
132.76	1.312	+ .001	0.00 Solid
136.10	1.921	+ .002	− .01 Solid
139.35	2.733	.000	.000 Triple point
144.521	4.477	+ .002	− .005 Liquid
148.960	6.635	+ .007	− .012 Liquid
152.549	8.939	+ .005	− .007 Liquid
156.699	12.380	.000	.000 Liquid
161.724	17.914	− .006	+ .005 Liquid
167.369	26.350	− .008	+ .005 Liquid
172.560	36.674	+ .005	− .002 Liquid
178.043	50.790	+ .002	− .001 Liquid
185.562	76.724	− .005	+ .001 Liquid

tion of gravity was taken as 980.665 cm/sec². The gravitational acceleration for this location, 979.973 cm/sec², was taken from the work of Sternewarte.[10]

The observations have been represented by the following equations: Solid phosphine from 128.67 to the melting point 139.35°K,

$$\log_{10} P_{(\text{int. cm Hg})} = -895.700/T + 6.86434. \quad (1)$$

Liquid phosphine from 139.35 to 185.56°K,

$$\log_{10} P_{(\text{int. cm Hg})} = -1027.300/T - 0.0178530T + 0.000029135T^2 + 9.73075. \quad (2)$$

The observed and calculated values are given in Table I. The boiling point was calculated from Eq. (2) to be 185.38°K.

The vapor pressure of liquid phosphine has been measured by Henning and Stock.[11] For corresponding pressures, the vapor pressure equation of Henning and Stock gives temperatures which are higher by the following amounts than those given by the above equation: at 150°K, 0.09°; at 160°K, 0.10°; at 170°K, 0.12°; at 178°K, 0.18°; at the boiling point, 0.27°. The two temperature scales have been shown to be consistent to 0.03° from 160°K to 195°K by the vapor pressures of HCl.[2] The higher temperatures given by Henning and Stock may be due to an impurity in their sample. The heat of vaporization calculated from the vapor pressure equation of this research is in better agreement with the calorimetric value than that calculated from the equation of Henning and Stock, which is evidence that their equation is somewhat in error near the boiling point.

[10] Landolt, Börnstein and Roth, *Physikalische-chemische Tabellen* (Verlag Julius Springer, Berlin, 1923).
[11] Henning and Stock, Zeits. f. Physik **4**, 226 (1921).

TABLE II. *Melting point of phosphine.*

DATE AND TIME	% MELTED	T°K RESISTANCE THERMOMETER	T°K THERMO-COUPLE	PRESSURE (int. cm Hg)
4/20/35 9:45 P.M.	Heated into melting point			
10:51 P.M.	9	139.321	139.31	2.730
4/21/35 12:04 A.M.	Supplied heat			
2:05 A.M.	12	139.333	139.32	2.730
2:45 A.M.	Supplied heat			
4:56 A.M.	20	139.343	139.35	2.731
5:26 A.M.	Supplied heat			
8:22 A.M.	30	139.347	139.35	2.733
9:08 A.M.	Supplied heat			
11:19 A.M.	40	139.346	139.36	2.735
12:01 P.M.	Supplied heat			
2:12 P.M.	65	139.350	139.35	
		Accepted values	139.35	2.733

MELTING POINT OF PHOSPHINE

Table II gives a summary of the observed melting point temperatures and pressures.

Table III contains a summary of measurements of the melting and boiling point temperatures for phosphine.

THE TRANSITION OF PHOSPHINE

Clusius[14] has measured the heat capacity of phosphine to the temperatures of liquid hydrogen. He found transitions at 88.5 and 30.3°K. He has published his heat capacity results only in graphical form. Two somewhat similar regions of high heat capacity are shown, one near 35°K and the other about 50°K.

The present investigation confirms the existence of the two transitions reported by Clusius and the region of high heat capacity at 35°K.

TABLE III. *Melting and boiling point temperatures of phosphine.*

MELTING POINT °K	BOILING POINT °K	OBSERVER
140.6	188	Olszewsky[12] (1886)
——	186.9	McIntosh and Steele[13] (1904)
——	185.65	Henning and Stock[11] (1921)
139.7	——	Clusius[14] (1933)
139.35	185.38	This research

[12] Olszewsky, Phil. Mag. (5) **39**, 188 (1895).
[13] McIntosh and Steele, Proc. Roy. Soc. **73**, 450 (1904).
[14] Clusius, Zeits. f. Elektrochem. **39**, 598 (1933).

However, we have found that another transition exists at 49.43°K. The previous observations below this temperature refer to an unstable modification. The small rise in heat capacity shown in Clusius' graph near 50°K indicates that one or two percent of the stable form was present during his measurements. All of the transitions have been carefully reinvestigated.

The Transition Temperature at 88.10°K

From cooling and warming curves it was found that phosphine can be superheated or supercooled one or two tenths of a degree above or below 88.10°K. Table IV contains a summary of the measurements.

The Transition Temperature at 49.43°K and the Rate of Transformation

When phosphine is cooled slowly below 49.43°K it undergoes a transformation to another form. If cooled with sufficient rapidity, the high temperature form may be completely supercooled and kept at liquid hydrogen temperatures with practically no conversion. On warming, the supercooled form begins to change spontaneously into the stable low temperature form at about 36°K. The rate of the transformation reaches a maximum at about 40°K and becomes too small to measure at 47°K. Complete conversion to the stable form requires two to three days near 40°K. Fig. 1 shows the variation of the rate of transformation with temperature. This is indicated approximately by a graph of the warming rates at various temperatures. The heat leak from the surroundings was negligible during the measurements, which were made with between 50 and 60 percent transformed.

Table IV. *The transition temperature at 88.10°K.*

Time	% Transformed	T°K Resistance Thermometer	Thermocouple
0	Cooled approximately half-way through the transition		
1:44		87.99	87.98
5:00	Cooled below the transition temperature and conversion completed		
5:30	Heat added		
8:12	17	88.20	88.20
8:23	Heat added		
13:36	33	88.22	88.23
13:51	Heat added		
17:20	50	88.25	88.24
17:28	Heat added		
20:35	67	88.31	88.34
20:43	Heat added. Transition complete		
24:34	Cooled partially back through the transition		
31:30		87.99	88.03
		Accepted value	88.10±.10°

Clusius[14] gives 88.5°K for this temperature.

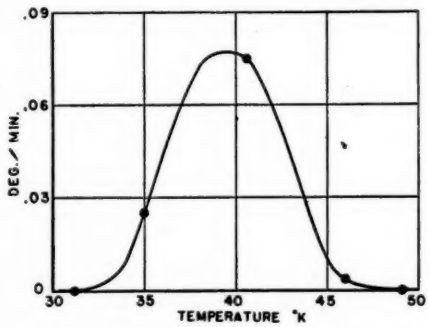

Fig. 1. Variation of the rate of transformation of phosphine with temperature ordinates: warming rate of the calorimeter in deg. per min. with 50 percent transformed.

To determine the transition temperature, sufficient energy was added to the low temperature form to cause approximately 50 percent conversion. The temperatures attained in three separate measurements were: 49.44°K, after an equilibrium period of 12 hours; 49.40°K, equilibrium period, 6 hours; 49.45°K, equilibrium period, 7 hours. The average of these values, 49.43°K, has been taken as the transition temperature.

The transition temperature could not be reached by allowing the supercooled phosphine to warm spontaneously due to the slow rate of conversion; the highest temperature reached in this way was 47.3°K. It was possible to heat the low temperature form 0.25° above the transition temperature before conversion began.

The Transition Temperature at 30.29°K

A transition occurred in the unstable form at 30.29°. No supercooling or superheating could be detected at this temperature. Table V contains a summary of the temperature measurements.

The Region of High Heat Capacity Near 36°K

Above the transition at 30.29°K the heat capacity curve shows an abnormal rise, followed by a rather abrupt decrease near 35.66°K.

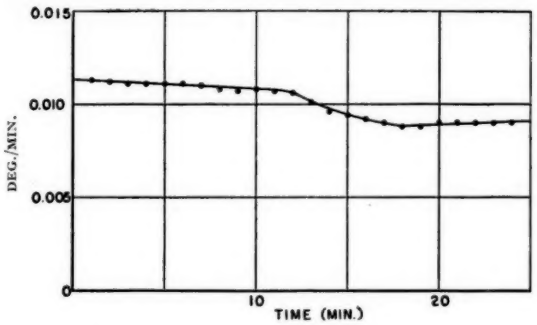

FIG. 2. Cooling rate curve for phosphine near 35.66°K. The temperature was 35.66°K at 15.5 minutes on scale.

Within the limit of accuracy of the observations there was no isothermal absorption of heat near the region of sudden change and for this reason the phenomenon was studied by means of cooling and warming rates near 36°K. When the rate of cooling or warming is plotted against time, a break is found at 35.66°K extending over the comparatively small region of ±0.03°. Fig. 2 shows one of these cooling curves.

The curve indicates that the heat capacity drops by approximately 15 percent within 0.06°, and no doubt this region would be smaller if the equilibrium were instantaneous. There is no indication of an isothermal heat effect, or of superheating or supercooling.

MEASUREMENT OF AMOUNT OF PHOSPHINE

The amount of phosphine used in the calorimetric measurements was determined in a thermostated bulb of about 5 liters capacity. The apparatus and procedure have been described[15] previously.

During the experiments, some of the same phosphine on which the calorimetric measurements were made was used by Long and Gulbransen[16] for their data of state measurements on this substance. From their data and Ritchie's[8] density measurements at 0°C we have calculated the coefficient, α, of deviation from Boyle's law at one atmosphere and 298.1°K to be -0.0074 per atmos where $PV=P_0V_0(1+\alpha P)$. In calculating this value we made use of the molecular weight 34.044 rather than the value 34.000 obtained by Ritchie and used by Long and Gulbransen in presenting their data. Essentially the calculation assumes that Ritchie's density measurements were correct but that the extrapolation of the PV product to zero pressure is in error. The molal volume of an ideal gas at 0°C=273.10°K and 1 atmos. was taken as 22411.5 cc. 2.446 moles of phosphine were used for the measurements.

[15] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).
[16] Long and Gulbransen, J. Am. Chem. Soc. **56**, 203 (1936).

HEAT CAPACITY OF PHOSPHINE

The heat capacity results are given in Table VI. For the calculation of energy, 1.0004 absolute joules were taken equal to 1 international joule and 4.185 absolute joules were taken equal to 1 calorie. The data are shown in Fig. 3.

Before Series III and IV were taken, the calorimeter was kept, in each case, near 40°K for 48 hours. Complete conversion was assured by the absence of any heat effect due to the transition in the unstable form at 30.29°K.

The heat capacities of the unstable form from 30.29°K to 35.66°K and the heat of transition

TABLE V. *Transition temperature of phosphine.*

DATE AND TIME	% TRANSFORMED	T°K RESISTANCE THERMOMETER	T°K THERMOCOUPLE
Series 1			
5/7/35 9:04 P.M.	Heated into transition		
9:17 P.M.	40	30.289	30.25
9:38 P.M.	Heat added		
10:01 P.M.	60	30.288	30.25
10:08 P.M.	Heat added		
10:40 P.M.	90	30.293	30.27
Series 2			
5/23/35 9:21 P.M.	Heated into transition		
9:48 P.M.	25	30.284	30.28
Series 3			
5/25/35 1:13 A.M.	Heated into transition		
1:27 A.M.	65	30.290	30.34
Series 4			
8/7/35 7:00 P.M.	Cooled partially through transition		
9:30 P.M.		30.275	30.33
		Accepted value	30.29

Clusius[14] gives 30.3°K for this temperature.

at 30.29°K depended to some extent upon the rate of cooling between 50 and 35°K. The rate of cooling before the measurements on the form unstable below 49.43°K is given in Table VII.

The discussion of the effect of different rates of cooling is given later.

A heat capacity measurement, which has not been given in Table VI, was made between 49.09 and 51.33°K at the end of Series I. This measurement was high because it included a heat effect due to the transition of a small amount of the stable form which was present. The data indicate that 1.6 percent of the unstable form had gone over to the stable modification. Most of this conversion took place during the heat capacity measurements from 36°K to 47°K; consequently, the measurements in this region for Series I may be in error by one or two percent.

It is estimated from the rate of transformation and the time of cooling that below 36°K, the high temperature form contained less than 0.2 percent of the stable modification for Series I, less than 0.1 percent for Series V and X, and less than 0.4 percent for Series VII.

The measurements of Series II were made after cooling only to 44.7°K. The absence of any heat effect at 49.43°K shows that the high temperature form underwent no appreciable conversion during these measurements.

TABLE VI. *Heat capacity of phosphine.* (*Molecular weight, 34.044; 0°C=273.10°K.*)

T°K	ΔT	C_p CAL./DEG./MOLE	SERIES	T°K	ΔT	C_p CAL./DEG./MOLE	SERIES
Form stable below 49.43°K							
15.80	2.615	1.076	IV	33.31	3.824	4.169	III
16.65	2.694	1.197	III	33.41	3.644	4.188	IV
18.63	2.955	1.562	IV	37.13	3.835	4.886	IV
19.49	2.993	1.679	III	37.29	4.075	4.893	III
21.71	3.175	2.090	IV	41.12	3.985	5.571	IV
22.66	3.340	2.259	III	41.50	4.432	5.602	III
25.04	3.525	2.692	IV	45.10	3.974	6.314	IV
26.00	3.404	2.847	III	45.86	4.291	6.469	III
28.62	3.667	3.300	IV	47.85	1.517	6.982	IV
29.94	3.333	3.550	IV	49.43	Transition		
Form stable above 49.43°K							
17.71	2.747	1.987	V	47.52	3.255	10.51	I
18.81	3.386	2.200	I	48.66	2.553	10.68	II
20.58	2.930	2.641	V	51.14	2.414	10.87	II
22.31	3.743	3.054	I	54.45	4.217	11.10	II
23.65	3.248	3.431	V	58.19	4.832	11.34	VI
24.77	3.898	3.776	VII	63.40	5.570	11.56	VI
25.55	2.776	3.992	I	68.77	5.203	11.75	VI
26.94	3.396	4.551	V	74.33	5.922	11.90	VI
27.62	1.803	4.827	VII	80.07	5.569	11.98	VI
28.06	2.201	5.040	I	85.25	4.841	12.22	VI
29.05	1.035	5.594	VII	88.10	Transition		
29.29	1.321	5.809	V	92.69	5.115	11.15	VIII
30.29	Transition			98.01	5.389	11.21	VIII
31.34	1.006	8.20	I	103.50	5.184	11.22	VIII
31.65	2.314	8.80	V	109.39	5.414	11.26	VIII
32.22	3.141	8.73	VII	114.96	5.193	11.32	VIII
32.31	0.944	8.65	I	120.28	4.998	11.38	VIII
33.46	1.360	9.38	I	125.82	4.772	11.53	VIII
34.21	2.817	10.16	V	131.27	4.573	11.57	VIII
34.55	0.822	10.25	I	135.72	4.063	11.69	VIII
34.84	2.136	10.55	VII	139.35	Melting point		
35.33	0.741	11.35	I	146.11	5.449	14.58	IX
35.66	Abrupt decrease in heat capacity			151.69	5.293	14.51	IX
36.12	0.844	9.61	I	157.11	5.175	14.47	IX
36.49	1.136	9.55	VII	162.43	5.040	14.46	IX
40.87	3.018	9.84	I	167.64	4.919	14.44	IX
44.17	3.499	10.18	I	172.71	4.798	14.45	IX
46.04	2.723	10.41	II	177.69	4.677	14.48	IX
				182.73	4.558	14.48	IX
				185.38	Boiling point		

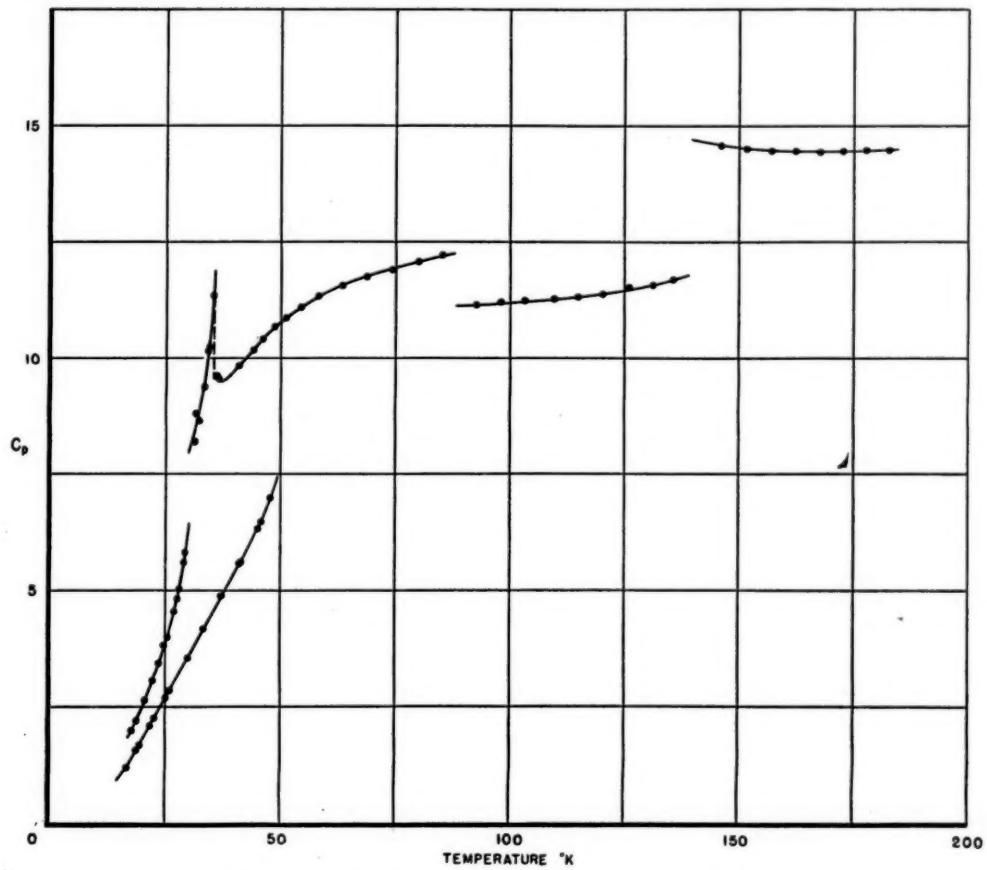

FIG. 3. Heat capacity in calories per degree per mole of phosphine.

Points taken from smooth curves through the data are summarized in Table VIII.

Another series of measurements was made from 15°K to 50°K after half of the phosphine had been allowed to undergo transformation to the stable form. These measurements were affected by the greater rate of conversion caused by the larger amount of the stable form present, and it was not possible to obtain results as accurate as those given for the other series. The results of this series will be discussed below.

A comparison of the results of Clusius[14] with those of the present investigation is not possible since the preliminary publication of his results is in graphical form.

THE HEAT OF TRANSITION AT 30.29°K

A summary of the measurements of the heat of transition at 30.29°K is given in Table IX.

The heat of transition was highest for the slowest rate of cooling in the above series. When the heat of transition is high, the heat capacity curve in the region from 30.29 to 35.66°K is correspondingly low. No heat capacities were taken in Series X, but the rate of cooling was the same as in Series V, so the heat capacity of that series was assumed in order to make the $\int C_p dT$ corrections. The small variations mentioned above produce a negligible effect in evaluating the entropy. In any case, the effect of the variation in the heat of transition is

TABLE VII. *Rate of cooling from 50°K to 35°K.*

SERIES	I	V	VII	X
T, °K		Time in minutes		
50	0	0	0	0
45	12	6	18	6
30	25	13	38	13
35	39	23	62	23

TABLE VIII. *Heat capacity of phosphine. Values taken from smooth curves through the data.*

T°K	C_p CAL./DEG./MOLE	T°K	C_p CAL./DEG./MOLE
Form stable below 49.43°K			
15	0.96	35	4.48
20	1.79	40	5.38
25	2.66	45	6.31
30	3.56		
Form stable above 49.43°K			
15	1.56	90	11.15
20	2.46	100	11.21
25	3.85	110	11.28
30	6.23	120	11.37
35	10.90	130	11.53
40	9.77	140	14.75
45	10.32	150	14.52
50	10.78	160	14.45
60	11.42	170	14.44
70	11.79	180	14.46
80	12.06	185	14.49

practically compensated by the change in the heat capacity. This is shown in Table X by separate entropy calculations made for three different series of measurements over this region.

The general character of the heat capacity curves between 25 and 35°K is of the type usually associated with molecular rotation in the solid state.

One measurement of the heat of transition was made on a mixture of 52 percent of the high temperature form and 48 percent of the stable form; the relative amounts were determined by assuming that the heat capacity of the mixture below the transition at 30.29°K is equal to the sum of the heat capacities of the two forms. The value obtained was 10.34 cal./mole of the mixture, or 19.8 cal./mole for 100 percent of the high temperature form.

HEATS OF TRANSITION AND FUSION

Table XI contains the results of the determinations of the heat of fusion and heats of transition at 49.43°K and 88.10°K.

THE HEAT OF VAPORIZATION OF PHOSPHINE

The heat of vaporization was measured by adding energy and accepting the gas evolved in the five liter measuring bulb referred to above. The pressure was kept constant to about a

TABLE IX. *Heat of transition at 30.29°K.*

TEMPERATURE INTERVAL	CORRECTED HEAT INPUT/MOLE	$\int C_p dT$	ΔH CAL./MOLE	SERIES
30.157–30.832	25.06	5.13	19.93	I
30.094–30.645	23.60	4.25	19.35	X
30.036–30.592	23.53	4.17	19.36	X
29.946–30.500	23.19	3.94	19.25	V
29.840–30.647	25.93	5.72	20.21	VII
		Average value	19.6±0.4	

Clusius[14] gives 19.5 cal./mole.

TABLE X. *Entropy change from 30.29°K to 35.66°K.*

SERIES	I	V	VII
Heat of transition/30.29°K	0.658	0.636	0.667
30.29°K–35.66°K	1.500	1.559	1.514
	2.158	2.195	2.181

TABLE XI. *Heat of transition and fusion of phosphine. Transition at 49.43°K*

TEMPERATURE INTERVAL	CORRECTED HEAT INPUT/MOLE	$\int C_p dT$	ΔH CAL./MOLE
49.076–50.209	196.52	11.03	185.5
48.639–51.138	210.04	24.26	185.8
	Accepted value		185.7±.2
Transition at 88.10°K			
87.652–89.625	137.96	22.49	115.5
87.555–89.271	135.51	19.74	115.8
87.482–89.725	141.46	25.70	115.8
87.372–90.009	146.13	30.22	115.9
	Accepted value		115.8±.1
Fusion at 139.35°K			
137.917–142.576	334.54	64.37	270.2
138.224–141.177	310.75	40.23	270.5
137.891–140.863	310.19	39.55	270.6
	Accepted value		270.4±.2

Clusius[14] has given 114.0 cal./mole for the heat of transition at 88.10°K and 267.3 cal./mole for the heat of fusion.

TABLE XII. *Heat of vaporization of phosphine, boiling point, 185.38°K.*

AMOUNT EVAPORATED, MOLES	TIME OF ENERGY INPUT, MINUTES	ΔH AT 760 MM. CAL./MOLE
0.20631	45	3486
0.21263	46	3489
0.21666	47	3486
0.21840	47	3491
0.21376	47	3490
	Accepted value	3489±3
From the vapor pressure equation of this research		3472
From the vapor pressure equation given by Henning and Stock[11]		3408

TABLE XIII. *The entropy of phosphine, molecular weight 34.044.*

	FORM STABLE ABOVE 49.43°K		FORM STABLE BELOW 49.43°K	
0–15°K, Debye function	$hcv/k=99$	0.495	$hcv/k=114$	0.338
Graphical	15–30.29°K	2.185	15–49.43°K	4.041
Transition	19.6/30.29	0.647	185.7/49.43	3.757
Graphical	30.29–49.43	4.800	—	—
Entropy at 49.43°K		8.13		8.14
Graphical, 49.43–88.10°K		6.705		
Transition, 115.8/88.10		1.314		
Graphical, 88.10–139.35°K		5.194		
Fusion, 270.4/139.35		1.940		
Graphical, 139.35–185.38°K		4.140		
Vaporization, 3489/185.38		18.82		
Entropy of actual gas at boiling point		46.25		
Correction for gas imperfection		+0.14		
Entropy for ideal gas at boiling point		46.39±0.1 cal. per deg. per mole.		

millimeter of mercury. A summary of the data is given in Table XII.

The heat of vaporization was calculated from the vapor pressure equations using the equation of state given by Long and Gulbransen.[16] This equation of state was corrected to the generally accepted molecular weight 34.044 rather than the value 34.000 used by the above authors.

THE ENTROPY FROM CALORIMETRIC DATA

An itemized account of the calculation of the entropy of phosphine is given in Table XIII. The entropy correction for gas imperfection was made by using Berthelot's equation of state, with $T_c=324.1$°K and $P_c=64$ atmos.[17]

The almost exact agreement of the entropies at 49.43°K for the two paths is undoubtedly fortuitous; the individual values may be in error by several hundredths of an entropy unit. The close agreement of the two values is an excellent verification of the third law of thermodynamics.

As mentioned above, one series of heat capacity measurements was made from 15 to 50°K with half each of the stable and unstable forms. The entropy value at 49.43°K, obtained from these measurements, agrees with the above value to 0.1 cal./deg. per mole. As the amount converted was measured in terms of the heat evolved during the partial transformation, the above entropy agreement is of interest in that it indicates that the process of conversion of the unstable to the stable form is accomplished by the formation of distinct phases. Since the character of the heat capacity curves of the two forms below 49.43°K indicates molecular rotation in the unstable form and no molecular rotation in the stable form, we had considered the possibility that the slow transformation at low temperatures might have involved the loss of molecular rotation in a gradual and homogeneous manner throughout the solid. The random distribution accompanying such a process would preclude an entropy agreement such as that given above.

THE ENTROPY FROM SPECTROSCOPIC DATA

Phosphine has a symmetrical pyramidal form, in which the principal moments of inertia $I_A=I_B\neq I_C$. The value $I_A=6.221\times10^{-40}$ gram cm² has been made certain by the measurements of Wright and Randall.[18] The value of I_C has not been determined experimentally, but Yost[19] has calculated a value of 8.26×10^{-40} gram cm² by making the plausible assumption that the bond angle is 100°. He then calculated $S_{298.1}=50.5\pm1.0$ for phosphine. The nuclear spin entropy, $R\ln 16=5.509$, is not included in this value.

By using the fundamental frequencies, 990, 1121, and 2327 cm^{-1}, observed by Fung and

[17] *International Critical Tables*, Vol. 3, p. 248.

[18] Wright and Randall, Phys. Rev. **44**, 391 (1933).

[19] Yost, J. Chem. Phys. **2**, 624 (1934).

Barker[20] and the frequency 2340 cm^{-1} calculated from valence forces by Howard[21] the entropy change of phosphine gas from 185.38°K to 298.1°K is found to be 3.96 cal./deg. per mole. This, added to the experimental value $S_{185.38}=46.39$, gives $S_{298.1}=50.35$ cal./deg. per mole, which agrees with the value given by Yost.

It is quite unlikely that any lack of equilibrium exists in the solid which would cause a discrepancy between the calorimetric and spectroscopic values, since the entropies given by the two paths below 50°K are in accord. The experimental value of the entropy of phosphine may therefore be used with confidence in thermodynamic calculations. In addition, the constants of the phosphine molecule may be obtained from the experimental entropy value, the familiar Sackur-Tetrode equation, and the value of I_A. For I_C, the value $7.9\times10^{-40}\pm0.8\times10^{-40}$ gram cm^2 is calculated; for the P−H distance, 1.45 ± 0.02A; and for the bond angle, $98\pm5°$. The value found for I_C definitely eliminates the possibility that phosphine is a spherical top, as suggested by Fung and Barker.

We thank Dr. Roy Overstreet for assistance with the experimental work.

[20] Fung and Barker, Phys. Rev. **45**, 238 (1934).
[21] Howard, J. Chem. Phys. **3**, 207 (1935).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

New Data on the H_2S Spectrum in the Photographic Infrared

The absorption spectrum of hydrogen sulphide gas in the region around 10,000A first reported by Cross[1] has been photographed under conditions rather closely approximating those of the first investigator. The absorption tube was 60 feet long. A 500 w projection lamp was used as the source. The gas in the tube was under a pressure of about $1\frac{3}{4}$ atmospheres. This pressure is higher than that used by Cross as it was found that at lower pressures, the absorption was too weak to be measured conveniently. Photographs were taken in the first order of a 21 foot concave grating giving a dispersion of 2.6A per mm. Eastman 1Q and 3Q infrared plates were used with exposures from 2 to 24 hours. The bands in this region are very weak and only the most intense lines appear definitely on the plates.

The following lines of the band around 10,100 cm^{-1} were measured.

10,168.1 cm^{-1}	10,128.5
10,160.6	10,123.5
10,149.3	10,116.9
10,141.0	10,110.6
10,135.7	10,103.9

Reliable measurements of lines beyond 10,168 cm^{-1} were not possible due to the presence of the strong water vapor band in this region.

The following lines, also reported by Cross, were the only ones observed between 10,013 and 10,216A; this conclusion is based on a study of ten spectrograms examined under various lighting conditions.

9983.8 cm^{-1}	9863.4
9980.9	9851.2
9977.5	9839.9
9973.7	9827.3
9968.8	9813.9
9964.0	9800.7
9958.5	9786.2
9952.4	
9945.7	
9938.7	

While there may be some doubt as to the presence or absence of the weak lines measured by Cross, the five strong lines that he observed at 9910.8, 9902.9, 9901.8, 9895.5 and 9875.5 cm^{-1} with intensities comparable to the other strong lines reported, are definitely missing. This result seems to disprove the previous[1] rotational structure analysis. The pronounced minimum in the center of the band classes the vibration as being along the middle moment of inertia.[2] This has to be parallel to the symmetry plane of the molecule because otherwise the angle between the two H−S bonds would be smaller than 88° 16′ (cf. Cross' calculations) which is highly unlikely from chemical consideration.

If we assume that the three fundamentals are approximately $\omega_\delta = 1236$, $\omega_\pi = 2615$, and $\omega_\sigma = 2632$ cm^{-1}, as seems fairly certain now particularly in view of the work of Bailey, Thompson and Hale,[3] the following parallel type bands would be expected in the region in question: $4\omega_\pi$, $4\omega_\sigma$, $2\omega_\pi + 2\omega_\sigma$, also combinations involving fairly high multiples of ω_δ. These high multiple ω_δ bands, however, have not been observed for any molecule so that we would not be justified in expecting them to appear with appreciable intensities for H_2S. The other three bands seem likely for the following reason. There seems to be no reason why the special type of electric moment observed for H_2O should hold for H_2S, so we would expect ω_π to appear in the infrared (as well as in the Raman effect) together with its overtones. The rather complicated structure observed around 3.7μ makes it likely that the bands there are a superposition of ω_π and ω_σ. No resonance between these two frequencies is to be expected for symmetry reasons. Furthermore, the statement of Bailey, Thompson and Hale that no even overtones of ω_σ should occur seems to be a misinterpretation of Weizel's[4] calculations which apply only to perpendicular type bands. In most molecules combinations of the type $2\omega_\pi + 2\omega_\sigma$ appear stronger than high overtones like $4\omega_\pi$ or $4\omega_\sigma$. The band around 9900 cm^{-1} might thus be due mainly to $2\omega_\pi + 2\omega_\sigma$ with a possible superposition of some other bands. Sufficient evidence is as yet unavailable to warrant any conclusions as to the classification of the band around 10,100 cm^{-1}.

FRANK D. CARVIN

Washington Square College,
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New York, N. Y.,
December 16, 1936.

[1] P. C. Cross, Phys. Rev. **47**, 7 (1935).
[2] Cf. Figs. 19 and 20 in Dennison's article on polyatomic molecules. Rev. Mod. Phys. **3**, 280 (1931).
[3] Bailey, Thompson and Hale, J. Chem. Phys. **4**, 625 (1936).
[4] W. Weizel, Zeits. f. Physik **88**, 214 (1934).

Further Relationships Between Absorption Spectra of Rare Earth Solids and Crystal Structure

The atoms in a solid are so close together that they exert powerful electric fields upon one another and thus cause a Stark splitting of the energy states of the atoms. The nature of the splittings will, of course, depend on the states involved, the symmetry of the surrounding atoms in the solid and on the nature and distances of the surrounding atoms. This problem has been treated theoretically by a number of investigators notably Bethe and Van Vleck. Penney and Schlapp[1] have treated the specific case of the splitting of the basic state of Nd^{+++} in a cubic field. They evaluated the constants in their equations so as to give the best fit with the experimental work of Gorter and de Haas[2] on the magnetic susceptibility of $Nd_2(SO_4)_38H_2O$. We were not able to locate the levels where they were predicted by that work. We did, however, find levels with the same relative separations, but with only about one-third the over-all separation. Evaluating the constants in Penney and Schlapp's equations from our levels, we calculated the magnetic susceptibility of the salt at various temperatures and obtained results in excellent agreement with the experimental results of Zernicke and James, S. Meyer, Selwood and others but not in agreement with Gorter and de Haas or Jackson.[3] Further, using the constants as determined for Nd^{+++} I calculated the levels for Er^{+++} and found excellent agreement with the levels determined spectroscopically by Nutting and Meehan.[4]

While any rhombic term in the potential equation should be easily detected experimentally since it causes splitting of a number of the levels, no such splitting was observed and we were forced to conclude that no rhombic field existed greater than two percent of the cubic field. The Nd^{+++} and Er^{+++} investigated are in monoclinic crystals. While one might expect that the octahedron of oxygens about the rare earth ion would give a field predominantly cubic, it seems astonishing that a rhombic term should not arise from the remaining atoms in the crystal. We are extending our investigation to include as many salts as possible. In view of the interesting results which we are obtaining it seems advisable to report some of them at this time.

The hydrated sulphates of the rare earths crystallize in a homologous series of the form $R_2(SO_4)_3\cdot 8H_2O$ and are completely isomorphic with each other. In these salts, which are monoclinic, the rare earth ion is presumably surrounded by an octahedron of oxygen atoms, four of which are part of water molecules and two of which belong to the sulphate. Dr. Howe and I have photographed the absorption spectrum of $Pr_2(SO_4)_3\cdot 8H_2O$ at various temperatures and found that the basic state is split into four levels in agreement with theory. Mr. Keller and I have also photographed $Pr_2(SO_4)_3\cdot 8H_2O$ containing a small amount of $Nd_2(SO_4)_3\cdot 8H_2O$ as an impurity. The basic state of Nd^{+++} is split exactly the same as in the pure $Nd_2(SO_4)_3\cdot 8H_2O$. The excited states are also split the same but are shifted to the violet by three or four wave numbers.

The chlorides of the rare earths form a homologous series of the form $RCl_3\cdot 6H_2O$. The crystals are also monoclinic and presumably have the six oxygens of the water molecules grouped around the rare earth ion in the form of an octahedron. One would, therefore, expect that the splitting of the states in the chloride and the sulphate would be the same. This was found to be true in the case of Gd salts.[5] One might expect it to be true in the case of Nd^{+++}, but if one examines the homologous series of the chlorides one finds that it ends at Nd^{+++} and that Pr^{+++}, Ce^{+++} and La^{+++} form chlorides containing $7H_2O$. The seventh water apparently enters a hole in the lattice brought about by the increasing size of the rare earth ion. In $Nd_2Cl_3\cdot 6H_2O$ this hole is almost certainly present but is not large enough to contain a water molecule. It will, however, permit the octahedron to expand into it slightly, and therefore, the crystal fields about the rare earth ion will be slightly weaker than expected and the over-all splitting of the basic state in the chloride will be less than in the sulphate.

Mr. Hamlin and I have photographed the spectrum of $NdCl_3\cdot 6H_2O$ and have found levels at 0, 62 and probably at 215 as compared to 0, 77 and 260 cm^{-1}, in the sulphate. We found no evidence of a rhombic field as the 62 cm^{-1} level was not split. Mr. Keller and I have photographed the absorption spectra of $PrCl_3\cdot 7H_2O$ containing Nd^{+++} as an impurity. Here the water occupies the hole in the lattice and we would expect the fields to be stronger. We found that the 77 cm^{-1} level was now shifted to 104 cm^{-1}.[6] The excited levels of these salts behave in a much more complicated manner and cannot be accounted for on the simple theories. There are too many lines in the multiplets so that some of them have to be of oscillational or vibrational origin. They are strongly evident in the case of Pr and are progressively less evident as the atomic weight is increased. Beyond Gd only a few, if any, can be of that type. We are extending these investigations to salts of Ho, Tm and Er and hope to have more results available shortly.

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Baker Research Fellow,
Cornell University,
Ithaca, New York,
January 14, 1937.

[1] Phys. Rev. **41**, 194 (1932).
[2] Leiden Commu. 278b.
[3] The experimental results on the magnetic susceptibility of $Nd_2(SO_4)_3\cdot 8H_2O$ are not satisfactory in that they do not agree among themselves. The low values obtained by Gorter and de Haas, and Jackson, which we do not check, also give an excellent fit with theory so that their relative values must be nearly correct. Perhaps the absolute values are in error. In any case more experimental work on this salt would be welcome.
[4] Phys. Rev. **50**, 574 (1936).
[5] J. Chem. Phys. **5**, 33 (1937).
[6] Drs. Meehan and Nutting have informed me privately that they also found that the lines of the other rare earths are markedly shifted when crystallized with $Ce_2(SO_4)_3$ salts which belong to a different crystal type.